CYBERNETIC METHODS IN CHEMISTRY & CHEMICAL ENGINEERING

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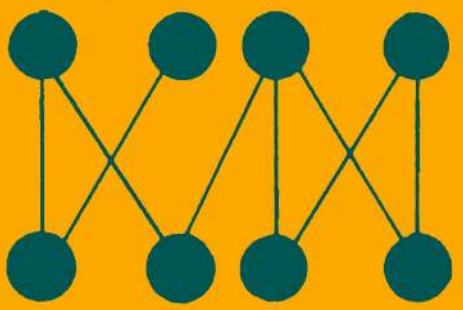
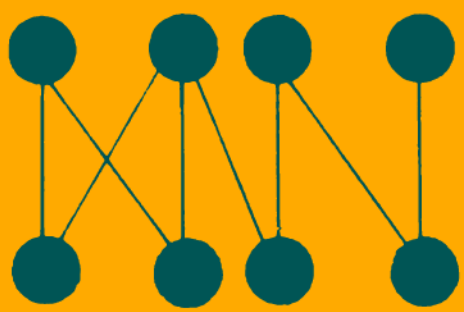


In a simple and fairly popular manner, the book presents the basic concepts of cybernetics, and describes its methods and tools (computers) as applied to chemistry and chemical engineering. Separate chapters are devoted to the principles of a cybernetic approach to the analysis of chemical-engineering processes and the development of new processes. A detailed consideration is given to the use of mathematical models for processes and typical reactors used in chemical engineering on the basis of reaction kinetics and heat transfer. Special mention is made of scale-up procedures and examples are given of optimum designs.

The book has been written as a study aid for students at chemical-engineering colleges or departments at polytechnic institutes. It may also be useful to research ers, engineers and technicians both at chemical factories and in R&D and design organisations.



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CYBERNETIC METHODS IN CHEMISTRY & CHEMICAL ENGINEERING

V. KAFAROV

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The Russian Alphabet and Transliteration

Аа	a	Кк	k	Хх	kh
Бб	b	Лл	l	Цц	ts
Вв	v	Мм	m	Чч	ch
Гг	g	Нн	n	Шш	sh
Дд	d	Оо	o	Щщ	shch
Ее	e	Пп	p	Ъъ	”
Ёё	e	Рр	r	Ыы	y
Жж	zh	Сс	s	Ьь	‘
Зз	z	Тт	t	Ээ	e
Ии	i	Уу	u	Юю	yu
Йй	y	Фф	f	Яя	ya

The Greek Alphabet

Αα	Alpha	Ιι	Iota	Ρρ	Rho
Ββ	Beta	Κκ	Kappa	Σσ	Sigma
Γγ	Gamma	Λλ	Lambda	Ττ	Tau
Δδ	Delta	Μμ	Mu	Υυ	Upsilon
Εε	Epsilon	Νν	Nu	Φφ	Phi
Ζζ	Zeta	Ξξ	Xi	Χχ	Chi
Ηη	Eta	Οο	Omicron	Ψψ	Psi
Θθ	Theta	Ππ	Pi	Ωω	Omega

На английском языке

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PREFACE

In the relatively short span of time that has passed since the appearance of the first (Russian) edition (in 1968), cybernetic methods have become predominant in the analysis and synthesis of chemical-engineering processes. To-day, there is hardly a single R & D laboratory or a chemical factory of importance where use is not made of mathematical modeling, the basic method of cybernetics, or computers, the basic tools of cybernetics.

Whatever the level in the hierarchy of chemical manufacture—from unit processes to departments and integrated factories, methods of cybernetics are being consistently used for process control, management and optimum planning. As a science, chemical engineering utilizes mathematical models for scientifically sound forecasts and optimization.

To keep pace with the changing world, some sections in the book have been rewritten. The revision has been especially considerable in the chapters on digital computers, automatic control of chemical-engineering systems, mathematical modeling of unit processes, analysis and synthesis of chemical-engineering systems and systems analysis. A section has been added on statistical models, experimental designs, and statistical optimization. New material has been added on stages in mathematical modeling, optimization (the geometric method), studies into micro- and macrokinetics, the design of a cascade of reactors under conditions of several micro- and macroscopic levels of mixing, etc.

CHAPTER I

BASIC CONCEPTS OF CYBERNETICS

Cybernetics may be defined as a *science dealing with any systems capable of perceiving, storing and processing information for the purposes of optimum control.*

Thus, cybernetics encompasses the concepts of a system, information, data storage and processing, system control and system optimization. Cybernetics widely employs mathematical models and seeks to obtain specific results so as to analyse and synthesize the systems under investigation and to predict their behaviour.

Since methods of cybernetics are applicable to any systems, they may as well be applied to chemistry and chemical engineering and implemented with computers—the tools of cybernetics.[1-6]

In our discussion we shall limit ourselves to engineering systems directly related to chemistry and chemical engineering.

I-1. SYSTEMS AND PROCESSES

Systems. Any system consists of interrelated components and is, in a sense, a closed entity; otherwise it would not be called a system. A *chemical system* is a collection of related physical and chemical processes and physical facilities that implement them. More specifically, a chemical system incorporates a chemical process (or processes) proper, an applicable reactor, and facilities to monitor and control the process and to provide links between the component units.

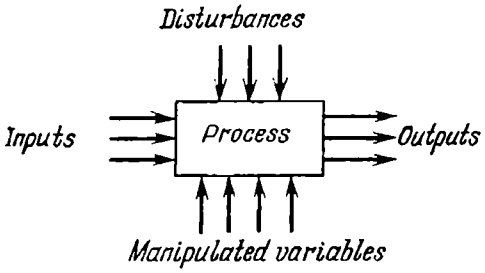


Fig. I-1. A simple controlled system

Any system has *inputs* and *outputs* (Fig. I-1). Inputs may be a source material, its composition, temperature,

etc. Outputs may be the finished product, its quality, temperature, and so on. A system is usually subject to *disturbances*, and in order to compensate them use is made of *control (or corrective) actions.*

Such a system may be exemplified by any controllable chemical process taking place in a controlled plant, or reactor (Fig. I-2). The progress of the process is monitored by a sensing element, SE; the signals of the sensing element are boosted by an amplifier, A, and applied to a signal converter, SC (which may be an electric-to-mechanical transducer). The converted signals act upon a controller, Cont, which feeds signals to a final control element, FC (which may be a valve on the line feeding the source material or heating agent). The signal from the controller causes the actuator either to increase or to decrease the amount of reactants or heating agent supplied.

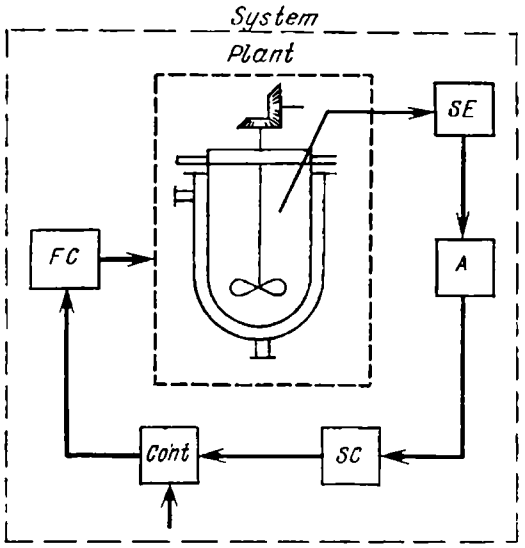


Fig. I-2. A controlled chemical process as a system

Arbitrarily, all systems may be divided into small-scale and large-scale systems.

A *small-scale* system is uniquely defined by the properties of the process and is limited to a single unit process, its internal constraints, and the reactor configuration.

A *large-scale system* is a collection of small-scale systems and differs from small-scale systems both qualitatively and quantitatively. The salient features of a large-scale system are (1) integrity, that is, the community of objectives and purpose; (2) large size and multiplicity of functions performed; (3) complex behaviour; (4) competitive aspects (conflicting processes may take place in a system, tending to reduce its effectiveness).[4] An example of a large-scale cybernetic system is a chemical department or a chemical factory.

Unit processes. Any chemical production sequence may be divided into a definite number of basic steps in which the basic processes common to all chemical engineering take place. Among the more important are: absorption, distillation, chemical reaction, etc.

A unit process associated with a specific chemical reactor constitutes a *controlled unit system.*

The basic feature according to which processes are placed under a particular heading is the identity of physical and chemical aspects, that is, the material and energy relationships within a given process. A unit process contains all the necessary and sufficient characteristics that single it out of the multiplicity of physical and chemical phenomena. The objective or purpose of a unit process is also taken into account.

According to their internal material and energy relationships, all processes

of chemical engineering are customarily divided into the following classes: hydrodynamic, thermal, diffusion, chemical and mechanical.

According to their objective or purpose and implementation, the above classes are divided into unit processes. For example, the diffusion class includes the following unit processes: absorption (desorption), distillation, extraction, adsorption (desorption), dissolution (crystallization), drying, ion exchange, etc.

All processes may be divided into deterministic and stochastic, or random.

A *deterministic process* is that in which the observables take on a continuous set of values in a well-defined (or definable) manner, while the output variable most representative of the process is uniquely determined by the input variable. Deterministic processes can adequately be described by the methods of classical analysis and numerical methods. An example of a deterministic process is that taking place in a continuous-flow, well-stirred reactor.

A *random (or stochastic) process* is that in which the observables change in a random manner and often discontinuously. In a stochastic process, the output variable is not directly related to the input variable. Stochastic processes are described in terms of statistics and probability theory. An example is a contact-catalytic process in which the yield of the product diminishes with decrease in the activity of the catalyst as it ages with time.

As regards most large-scale chemical systems, the prevailing trend is to replace the univalued determinism with a more flexible and multivalued stochastic or probabilistic approach. This trend sets the more recent physical sciences (quantum physics, for example) apart from the classical sciences (Newtonian mechanics). There is quite a number of publications on this subject.[4] This trend has been stimulated by the fact that instead of simple systems and single events we are now concerned with complex systems and mass phenomena where the outcome of an individual event is not so important as the general effect of the main body of events.

System hierarchy. Any chemical manufacture may be visualized as a sequence of three basic steps, namely, preparation of the source material, chemical treatment proper, and separation of the end products. This sequence is embodied in an *integrated chemical-engineering system.* A present-day chemical factory, as a large-scale system, consists of a great number of interrelated subsystems arranged in a three-level hierarchy (Fig. I-3). The subsystems at the lower level share between them the functions assigned to the subsystem at the next higher level. Each subsystem of a chemical factory is a combination of a chemical-engineering system and an automatic control system operating as a single entity designed to turn out a specified finished or semifinished product.

The lowest level in the hierarchy structure of a chemical factory comprises *unit processes* of chemical engineering (mechanical, fluid-flow, heat-transfer, diffusion and chemical) associated with suitable reactors and *local control systems.* Each unit process together with a particular reactor, or a well-defined and integrated collection of unit processes may be treated as a system

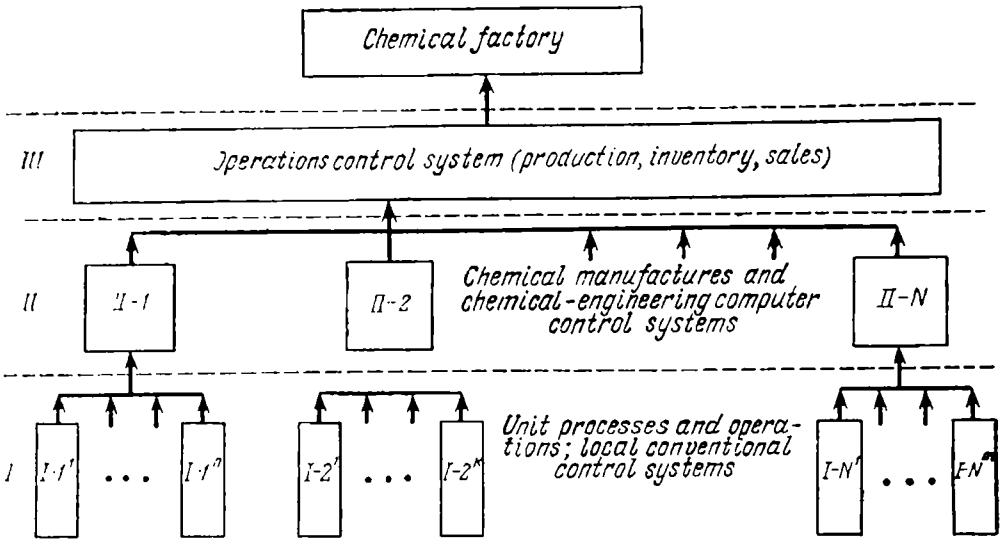


Fig. I-3. The hierarchy of chemical manufacture

or a subsystem in its own right, having certain inputs and outputs (see Fig. I-1).

Inputs, or *input variables*, are the quantitative characteristics (flow rate, composition, temperature, and so on) of source materials; outputs, or *output variables*, are the quantitative characteristics (flow rate, composition, temperature, etc.) of finished products and wastes of chemical processing.

In the analysis of a system, the input variables are divided into disturbances and manipulated variables. The variables associated with disturbances give a quantitative measure of external and internal disturbances (changes in the flow rate and composition of the source material, temperature variations in reactors, etc.) to which any system is always subjected and which tend to oppose the purposeful course of the process and force it away from the specified direction. The *manipulated variables*, which give a quantitative measure of the control actions of the system (changes in the flow rate, composition and other characteristics of the feed), are applied to the system so as to keep the output variables within the specified (set-point) limits in the face of disturbances.

Unit processes associated with a particular reactor design are most often deterministic systems. At the lowest level of a chemical factory, the information describing operation of the subsystems is enriched structurally, and control of the subsystems reduces mainly to *local stabilization* of the process variables.

The second level (see Fig. I-3) of a chemical factory comprises *production departments* and their associated *automatic control systems*. A department in a chemical factory is a collection of interrelated unit processes and reactors whose operation is accompanied by random disturbances; that is, the input-output relations of the subsystems become stochastic. In an analysis of the subsystems at the second level, one has therefore, to resort to techniques of

statistics and probability theory. The more important among them are Markov analysis, graph theory, and waiting-line theory. At this level, information is enriched statistically, and control of the subsystems involves optimization and programming for proper reactor coordination and for optimum load sharing.

The topmost level in the hierarchy of a chemical factory (see Fig. I-3) provides *management control for all production, management, inventory planning and marketing*. At this level, information is enriched semantically, and the need arises for situation analysis and optimal control of the entire factory. This involves the use of mathematical models, systems engineering, game theory, information theory, operations research, and waiting-line theory that can be handled only by specialists in these respective fields.

I-2. MODELING

A major distinction of present-day chemical-engineering processes which proceed at high rates, high temperatures, and high pressures in multi-phase systems is utmost complexity.

This complexity manifests itself in the multiplicity and diversity of process variables and the ramified internal relationships between them because of which a change in one variable may bring about nonlinear changes in other variables. This complexity grows still more formidable in the case of multiple feedback loops (page 28), and competitive courses for the process that may change its overall pattern. On top of all, random disturbances are superimposed on the process.

The external potential of information about chemical-engineering processes is very high. So that this information can be handled by the very narrow channels of perception, we are forced to reduce this potential and to limit the choice of alternatives. This can be done by gaining an insight into a particular process through models. A *model* is a simplified representation of those aspects of an actual process that are being investigated. The flow of information is broken into two stages; in the first stage, a model is compared with the real process, and it is taken to be adequate if the discrepancy is negligible; in the second stage, we compare our expectations with indications of the model. This procedure is called *modeling*. There is *physical modeling* and *mathematical modeling*.

(A) PHYSICAL MODELING

In this case, the process of interest is reproduced on different scales, and the effect of physical features and linear dimensions is analysed. The experiment is carried out directly on the real process. Experimental data are reduced to relationships involving dimensionless groups made up of various combinations of physical quantities and linear dimensions. With this dimensionless presentation the found relationships can be generalized to classes of events having the same dimensionless groups, or similarity criteria. These

dimensionless groups are derived on the basis of differential equations or dimensional analysis.

Physical modeling consists in seeking the same or nearly the same similarity criteria for the model and the real process. As already noted, the real process is modeled on a progressively increasing scale, with the principal linear dimensions scaled up in proportion (the similarity principle).

Thus, a physical model is strained directly within the system where the real process of interest takes place. This approach requires that the process be modeled up to the commercial scale, along with the complex systems that one has to deal with in chemical engineering.

For relatively simple systems (for example, single-phase fluid-flow or heat-transfer systems) the similarity principle and physical modeling are justified because the number of criteria involved is limited. With complex systems and processes, however, described by a complex system of equations, one has to deal with a large set of similarity criteria which are not simultaneously compatible and, as a consequence, cannot be realized. The similarity principle has proved its worth in analysis of deterministic processes which obey the laws of classical mechanics and proceed in bounded single-phase systems (as a rule, within solid walls). However, physical similarity is difficult to apply to an analysis of probabilistic processes involving multi-valued stochastic relationships between the events, and, notably, to an analysis of two-phase unbounded systems and to processes complicated by chemical reactions.[7]

(B) MATHEMATICAL MODELING

This method involves the use of mathematical models, or qualitative and quantitative representations or abstractions of real processes in mathematical symbols.

In building a mathematical model, a real process is reduced to its bare essentials, and the resultant scheme is described by a mathematical formalism selected according to the complexity of the process.

The choice of a model and whether or not it represents the typical features of the process in question may well mean the success or failure of an investigation.

A good model should reflect all the most important factors affecting the process, but it must not be crowded with minor, secondary factors which will only complicate mathematical analysis and might render the investigation difficult to evaluate.

Depending on the process under investigation, its mathematical model may be a system of finite or differential equations or both.

Using an applicable *algorithm*, one can readily derive the definable variables from the model equations and establish relationships to the defining variables for any set of values.

It is important that a model should represent with sufficient accuracy both the quantitative and qualitative properties of the prototype process; in other words, the model should adequately fit the real process. For a check

on this requirement, the observations made on the process should be compared with the predictions derived from the model under identical conditions.

Thus, a mathematical model of a real chemical process is a mathematical description combining experimental facts and establishing relationships between the process variables. For this purpose, it utilizes both theory and experiment. The final objective of a mathematical model is to predict the behaviour of the process and to work out recommendations to control its course. Where one is lacking information about a process or a system, one begins with the simplest models taking care not to distort the basic (qualitative) aspects of the prototype process.

From the foregoing it follows that mathematical model analysis involves three steps, namely: (1) formalization, that is, mathematical description of the process under investigation; (2) development of an algorithm of the process; (3) testing of the model and the solution derived from it.*

With mathematical model analysis, the model itself is strained through simulation on a computer, rather than within the real process or plant, as is the case with physical modeling. For this purpose, the variables that can affect the course of the process are changed from the computer control console to a predetermined program (algorithm), and the computer presents the resultant outputs.

With a conservative capital outlay, mathematical model analysis coupled with present-day computers makes it possible to investigate various plant configurations, to trace process behaviour under different conditions, and to find ways and means for improvements. Furthermore, this approach always guarantees an optimum solution within the framework of the model being used.

It should be stressed, however, that mathematical model analysis is in no way set to oppose physical model analysis. Rather, the former is to supplement the latter with its wealth of mathematical formalism and numerical analysis. In fact physical model analysis has at its basis the identity of a mathematical description for the processes in the plant under investigation and in its physical model. However, physical model analysis ignores the specific properties of the mathematical description; what it seeks is to establish similarity between the prototype plant or process and its model on the basis of certain defining groups in the common mathematical equations.

At present, a new aspect has been added to physical model analysis. Now it is used to establish the limits of strain for the coefficients entering the model equations, and through this, to scale down the modelled process and to test the model for adequacy.

Mathematical model analysis is applied to processes that can be described mathematically. According to the completeness of mathematical description,

* In greater detail, the methodology of mathematical model analysis is described on page 123.

there may be two limiting cases, namely: (a) the investigator has a complete system of equations describing all basic aspects of the process and all numerical values of the variables in these equations; (b) a complete mathematical description of the process is not available. This latter case is typical of cybernetical problems where one has to deal with control, having only incomplete information about the system and disturbances. In such cases, the task of model analysis has to be tackled along with that of model building—an aspect which sets this case widely apart from processes described mathematically.

In mathematical model analysis, a process is simulated on a computer by causing changes in the variables interlinked in a mathematical model. With this technique, all promising alternatives can be simulated to obtain an optimum model and, as a consequence, to optimize the process itself within a relatively short time. Mathematical modeling takes less money and time than physical modeling.

Mathematical model analysis also utilizes the principle of analogies, or correspondence between different physical phenomena, described by analogous mathematical equations. Several such phenomena and their equations are given below:

energy transport (force of friction)

$$\tau = -\mu\, dw/dx \qquad \text{(Newton's law)}$$

heat transport (heat flux)

$$q = -\lambda\, dt/dx \qquad \text{(Fourier law)}$$

mass transport (mass flux)

$$q_m = -D\, dc/dx \qquad \text{(Fick's law)}$$

transport of electricity

$$i = -\frac{1}{\rho}\, dV/dx \qquad \text{(Ohm's law)}$$

As is seen, each of the above equations contains a gradient, namely the velocity gradient dw/dx, the temperature gradient dt/dx, the concentration gradient dc/dx, and the voltage gradient dV/dx. It is obvious that with properly chosen conversion coefficients, transport of electricity can be used as an analogue, that is a model, of any of the above physical phenomena.

On the basis of analogies, the solution of one problem can throw light on the properties of a whole class of systems described by analogous mathematical equations. The findings of a study into one group of systems can give insight into others, although they may belong to entirely different fields of science and technology. This possibility is a very important outcome of mathematical modeling. Analogies form the basis of operation for analog computers in setting up and interpreting physical and chemical processes widely differing in nature.

Basic types of mathematical models. The choice of a particular type of mathematical model is determined by the specific conditions under which a given process can proceed in the selected reactor.

Where the basic process variables vary with both time and space or if these changes occur only with space of a dimension exceeding unity, such processes are represented by *distributed-parameter models* which are formalized as partial differential equations.

With the basic process variables varying only with time, such processes are represented by *lumped-parameter models* which are formalized as ordinary differential equations.

Chemical-engineering processes are remarkable for their complexity. This complexity manifests itself in the wealth of information contained in such systems and in the mutual effect of the process variables. This is why, with such processes, it is convenient to construct mathematical models separately for individual areas (the block-diagram principle), as this greatly simplifies their simulation on computers. In each specific case, a complete model of a process is obtained by combining the models of the individual areas (blocks). Schemes for breaking up a complete model into blocks will be discussed later, after an introduction to the use of computers.

The primary objective of cybernetics is to control a given system or process. As a consequence, a complete mathematical model is expected to describe relationships between the basic process variables under steady-state conditions (a static model) and under transient conditions (a dynamic model).[7]

Static model. A static (or steady-state) model ignores changes in process variables with time. Before a static model is constructed, the process is analysed to establish its physical and chemical nature, its objective, the governing equations describing a given class of processes, and also the specific features of the process as a unit process.

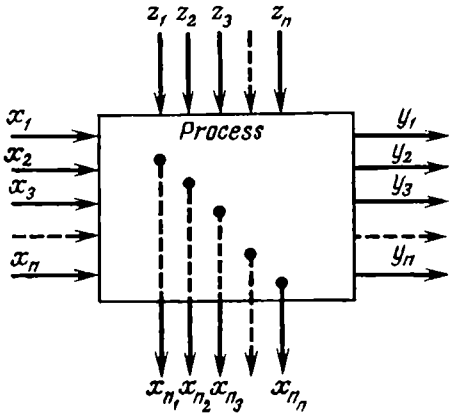


Fig. I-4. Input and output process variables

$x_1, \ldots, x_n$ – manipulated variables; $x_{n_1}, \ldots, x_{n_n}$ – intermediate variables; $y_1, \ldots, y_n$ – controlled variables; $z_1, \ldots, z_n$ – disturbances

Then the input and output variables of the process are ascertained (Fig. I-4). These include variables which change with the progress of the process (*controlled variables*), variables which directly affect the course of the process and which can be measured and changed purposefully (*manipulated variables*); variables which directly affect the course of the process, but which cannot be changed purposefully (*disturbances*); variables related to the course of the process only indirectly (*intermediate variables*). After that, relationships, constraints and boundary conditions for the process are established.

The static model of a unit process should allow for all possible modes of operation of the typical reactor.

Dynamic model. The construction of a dynamic (or unsteady-state) model reduces to obtaining so-called dynamic characteristics of a process, that is, to establishing relationships between its main variables as they change with time. Dynamic characteristics can be obtained by theory, by experiment, or both.

In obtaining dynamic characteristics experimentally, disturbances are applied to the input of the system under investigation, and the time response to the disturbance is noted. Such experiments are based on the laws of signal flow dealt with in information and control theory (see below).

A dynamic model of a process may take the form of a set of transfer functions relating the selected dependent variable to one or several independent variables, ordinary or partial differential equations derived theoretically and containing all the necessary dependent and independent variables, or equations derived for the various elements of the unit process that may be analysed independently of one another.

A *complete mathematical model* of a process combines the basic process variables, relationships between the basic variables under static or steady-state conditions, constraints, optimality criteria, objective functions, and also relationships between the basic variables under dynamic or unsteady-state conditions.

In diagrammatic form, the various steps in constructing a complete mathematical model are shown in Fig. I-5.

Rigid and probabilistic models. Depending on whether a given process is deterministic or stochastic, it may be represented by any one of the following mathematical models:[4] an analytical rigid model, a numerical rigid model, an analytical probabilistic model, or a numerical probabilistic (Monte Carlo) model.

It may be added, though, that in some practical cases a model cannot be classed under any of the above headings. The choice of a particular type of model is to a great extent determined by the simplicity of solution it offers.

Rigid models (analytical and numerical) usually describe deterministic processes without the use of probability distributions. This does not mean to say that the underlying phenomena, especially when a numerical rigid model is used, are not statistical in character. What is meant is only that we choose to deal only with averages and not with whole distributions.

Probabilistic models (analytical and numerical) usually represent stochastic processes.

In constructing rigid models, we utilize different classical techniques of mathematics, namely differential equations, linear difference equations, integral equations, and operators for conversion to algebraic models. Probabilistic models represent the distribution of discrete and continuous variables and also sample distributions.

A major advantage of statistical models over analytical ones is that they do not call for rough approximations and allow for a greater number of

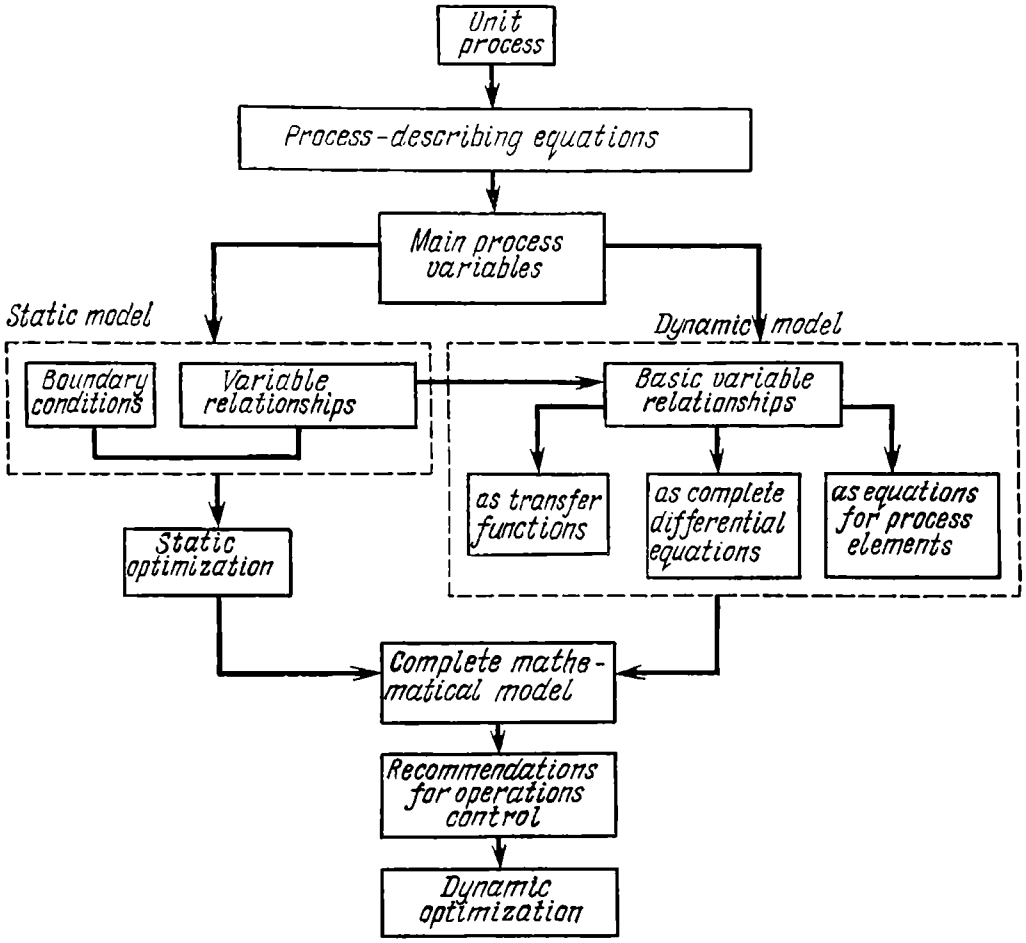


Fig. I-5. Stages in the development of a complete mathematical model for a process

factors. Unfortunately, such models are much more difficult to analyse and grasp. From this point of view, it may be preferable to use less precise analytical models. The best results are obtained when both analytical and statistical models are used jointly: a simple analytical model will give an insight into the basic behaviour of the prototype system and suggest further approaches in which statistical models of any complexity may be used.

The "black box" principle. In cybernetics, this principle is employed when, in an analysis of complex processes, one cannot establish internal relationships within the system. Because of this, the object under study, appears to be enclosed in a container, the so-called "black box" to which we, as observers, have incomplete access. With this principle, a mathematical description concerns only with the dependence of outputs on the inputs and ignores the interior structure of the process.

The concept of the "black box" is a pivotal one in cybernetics as it provides a useful mathematical approach to the behaviour of complex systems, that is, to their responses to various external stimuli while divorcing

from their internal structure. Many systems, especially large ones, are so complex that even with perfect information about the state of their components, it cannot practically be related to the behaviour of the system as a whole. In such cases, the matter can greatly be simplified by representing a complex system as a "black box" model which functions in the same manner as the system. Analysing the behaviour of the model and comparing it with that of the system, one can derive a number of conclusions as regards the properties of the system, and if the model adequately fits the prototype system, one can select a working hypothesis about the internal structure of the system.

The "black box" principle proves extremely useful when one system has to be replaced with another functioning in a similar way. For example, in the automatic control of hazardous chemical manufacture the need arises to replace the human operator with an automatic device capable of performing the same functions.

I-3. AN OUTLINE OF INFORMATION THEORY

Information and its quantitative measure. In defining a system, we have stated that it consists of individual elements. The lines interconnecting the individual elements of a system (see Fig. I-2) are in effect communication links over which information is exchanged between the elements. Accordingly, each element of a system has an input and an output. Thus, cybernetically, a system is a closely knitted information network rather than a collection of isolated elements.

What is then information and how can one measure it quantitatively?

Information is any data for which the primary source is experience or observations.*

Complex phenomena which also include many chemical-engineering processes are extremely diverse in their internal relationships and are subject to stochastic changes. Therefore information about such processes may be expressed statistically in the expectation that they will take a definite course. Or, which is the same, information is expressed in probabilistic forms.

If an experiment may have N different outcomes, of which n outcomes are favourable, then the probability of a favourable outcome is

$$P = n/N \tag{I-1}$$

According to Eq. (I-1), the probability is a fraction. Since however a quantitative expression for information is a ratio of probabilities, one would have to deal with unwidely multitier fractions. To avoid this, use is made of logarithms of probabilities. Then multiplication and division of quantities is reduced to the addition and subtraction of their logarithms.

* This definition is not claimed to be a universal one and is given only for purely applied purposes in the calculation of chemical-engineering systems.

Accordingly, a measure of information is defined as the ratio of the logarithm of the probability after reception of information (P_1) to the logarithm of the probability before reception of information (P_2):

$$i = \log_2 P_1 / \log_2 P_2 \tag{I-2}$$

with the logarithms taken to the base 2.

The unit of information is the binary digit or *bit*, equal to one binary decision or the designation of one of two equally probable values or states (such as "0" and "1") of anything used to store or convey information. Preference has been given to the binary number system instead of the more usual decimal notation because of the ease with which it can be realized technically. There is, however, a deeper motive behind this choice.

Norbert Wiener,[1] one of the founders of cybernetics, has defined it as "the science of control and communication in the animal and the machine". It has been established that the nerve circuits in man, consisting of nerve cells (neurons), are similar in structure to communication links in engineering systems.

In fact, similar processes take place in the nerve circuits and the communication links: information is accumulated and processed discretely, on the "yes-no" principle. Like the flip-flops (storage elements) of a computer, the nerve cells can only exist in one of two states, excited or unexcited, which corresponds to the ON and OFF states. Obviously, it is simpler to build a computer which recognizes two states than one capable of recognizing ten states, or ten symbols of the decimal number system.

These are the reasons why the binary number system has come to be used both in the evaluation of information and in computers. In either case, use is made of only two symbols, "1" and "0", and all numbers are combinations of the two symbols.

A decimal number can readily be converted to its binary form. For this conversion, the decimal number is divided by the base of the binary number system, that is 2, and the result and remainders after subtraction are written out, beginning with the last result.[25]

Example I-1. The decimal number $34 = 4\times10^0+3\times10^1$ may be converted to a binary number as follows:

$$\begin{array}{r|l}
34 & \\
\hline
0 & 2 \\
\hline
17 & 2 \\
\hline
1 & 8 \quad 2 \\
\hline
0 & 4 \quad 2 \\
\hline
0 & 2 \quad 2 \\
\hline
0 & 1
\end{array}$$

Thus, in binary notation, the decimal number 34 is 10010.

The procedure for converting a number from binary to decimal is simple: the symbols of the binary number are written separately in the reverse order, each is multiplied by 2 raised to the succesive powers, and the results are added together:

$$0\times2^0+1\times2^1+0\times2^2+0\times2^3+0\times2^4+1\times2^5 = 34$$

Among the advantages of the binary number system are simplicity of computations and convenient use of combinational logic because all algebraic variables in binary notation take only two numerical values, 0 and 1. Using binary notation, the English mathematician George Boole devised a mathematical system called Boolean algebra after him.

Several examples of computation in binary notation follow.

Example I-2. Multiplication and addition of single-digit binary numbers may be tabulated as follows:

multiplication

$$0\times0 = 0 \qquad 1\times0 = 0$$
$$0\times1 = 0 \qquad 1\times1 = 1$$

addition

$$0+0 = 0 \qquad 1+0 = 1$$
$$0+1 = 1 \qquad 1+1 = 10$$

In decimal notation, the last sum would be $1+1=2$. In the binary number system, however, 1 plus 1 is 0, and 1 to carry. Therefore we write 0 and carry 1 to the next higher digit position.

As a measure of information, Claude Shannon[8] in 1948 derived an information entropy equation similar to Boltzmann's entropy equation:

$$i = -(P_1 \log_2 P_1 + P_2 \log_2 P_2 + \ldots + P_m \log_2 P_m) = -\sum_{j=1}^{m} P_j \log_2 P_j \qquad (I\text{-}3)$$

where $P_1, P_2, \ldots, P_m$ are the probabilities of events 1, 2, ..., j.

The " $-$ " sign on the right-hand side of Shannon's equation indicates that all terms $P \log_2 P$ are non-positive. The probability P, if it is not equal to zero, is a positive number not exceeding 1, that is, $\log_2 P$ is a negative number or zero, and, as a consequence, the product $P \log_2 P$ will also be a negative number or zero. Thus, the " $-$ " sign makes the right-hand side of this equation positive.

It follows from Eq. (I-3) that information is additive, that is, the total information is equal to the sum of the information held by the individual events enclosed in parentheses. Thus, the information entropy equation describing a set of events and their probabilities gives the outcome of that set of events. In other words, any uncertainty as to the outcome of the events is removed, or, which is the same, information may be regarded as a *measure of orderliness of the system.*

As an example, we shall consider three limiting cases:

1. Assume that an event will occur with certainty, that is, its probability is unity ("temperature will rise on heating"). Then

$$i = -(1 \log_2 1 + 0 + \ldots + 0) = 0$$

that is, the system contains no uncertainty, and a message about its test carries no information.

2. If a single event has zero probability, it carries no information either ("in the absence of chemical interaction, the composition will not change"), because

$$i = -0 \log_2 0 = 0$$

3. The largest amount of information is carried by equiprobable events ("in the presence of chemical interaction, the temperature within a reactor is distributed uniformly"), that is, when $P_1 = {}^1/_2$, then $P_2 = {}^1/_2$ as well, because

$$i = -\left(\frac{1}{2} \log_2 \frac{1}{2} + \frac{1}{2} \log_2 \frac{1}{2}\right) = 1$$

Signals. Information in systems is transmitted as signals which may be mechanical motion, heat, flow of matter, electricity, sound, light, radio waves, and other manifestations of natural forces. The form of a signal is always chosen to be compatible with the system intended to receive and execute it, because the system supplies the energy necessary to execute the signal.

Signals always flow in a certain definite direction such that in a system consisting of a number of elements each element is a signal source with respect to the next element which now appears as a signal receiver but also acts as a signal source for the next element. The flow of signals is illustrated in the diagram of Fig. I-2.

As is seen, the signal flow is always in one direction: the input variable of an element is always the cause for a change in the condition, and the output variable is always its effect, and they cannot change places. Thus, the direction of signal flow cannot be reversed.

The signal sources and receivers used in a system, together with the intervening transmission medium, make up the *transmission* or *communication channel* of that system. Thus, signals carry information over communication or transmission channels.

Standard elements of a system. The manner in which an element handles signals passing through it (called the *response* of that element) depends on its properties. On the basis of response, all the multitude of elements used in different systems may be reduced to a limited number of standard elements. Conversely, an element may be evaluated quantitatively and its mathematical model may be constructed by comparing its response with that of a standard element.

In deriving a mathematical model of an element by this *stimulus-response*

technique (also known as *response analysis testing*), it is customary to subject the element to any one of three tests, each using a test signal (stimulus, excitation or disturbance) of its own as follows:

(1) The step function test: the input variable (usually, the concentration of a tracer material in the feed stream to the system) is raised to a new value stepwise, and the transient response is observed at the system exit. It is called the *step function response* (or simply the *step response*), or the *F*-diagram (Fig. I-6*a*).

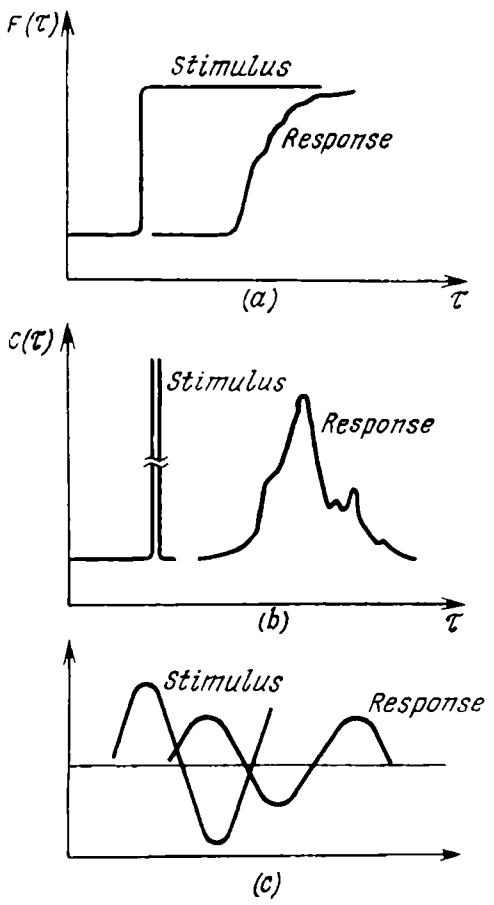


Fig. I-6. Test signals and responses
(*a*) step input and response (*F*-diagram); (*b*) impulse input and response (*C*-diagram); (*c*) sinusoidal input and response

(2) The impulse function test: the input variable is subjected to a sudden, impulse change (an amount of a tracer is injected instantaneously into the feed stream); the response observed at the system exit is called the *impulse function response* (or simply the *impulse response*) or the *C*-diagram (Fig. I-6*b*).

(3) The frequency response test: a sinusoidal disturbance is introduced into the system, and the system response is recorded at the system exit. The *frequency response* is likewise a sinusoid, but with an amplitude and a phase changed by the behaviour of the element (Fig. I-6*c*).

Consider the *F*-diagrams, or the step function responses, of basic standard elements. Let x designate the unit step input, y the output, and τ the time.

A pure-gain element. This type of element is also called amplifying, non-capacitive, or proportional. For such an element, the output signal is proportional to the input, that is,

$$y = Kx \qquad \text{(I-4)}$$

where K is a proportionality coefficient, or the gain of the element (see page 31).

A $y-\tau$ plot yields a straight line (Fig. I-7*a*), which implies that a step change in the stimulus (input) brings about likewise a step change in the response (output).

A time-lag element. This type of element is also known as aperiodic, single-capacitance, static, or relaxation. In this case, a step change in the stimulus (input) causes the response (output) to tend to a new steady-state value aperiodically (exponentially) (Fig. I-7*b*). Such an element is described by

the following equation

$$y = Kx(1 - e^{-\tau/T}) \tag{I-5}$$

where T is the time constant determined by the capacitance V and throughput V_s of the element (see page 31).

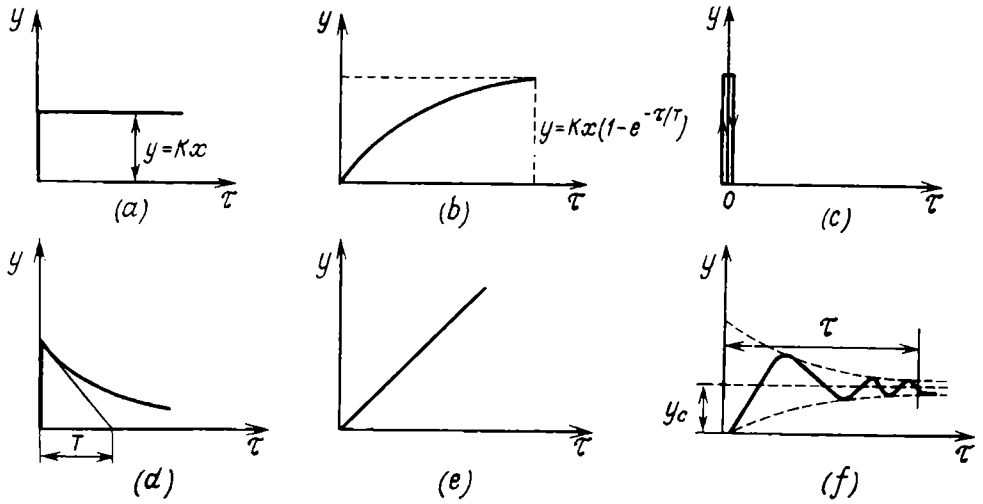


Fig. I-7. Responses of standard system elements to a step input
(*a*) pure-gain element; (*b*) time-lag element; (*c*) differentiating element; (*d*) time-lag differentiating element (real differentiator); (*e*) integrating element; (*f*) oscillatory element

The relaxation type of element is characteristic of most chemical-engineering processes which respond to input disturbances with a time lag (for example, stirred reactors, tanks, etc.). A relaxation element is identified with the so-called well-stirred tank model (see page 111).

A differentiating element. For an ideal, distortion-free differential element, the output signal $y(\tau)$ is the time derivative of the input:

$$y(\tau) = dx(\tau)/d\tau \tag{I-6}$$

Since the derivative of a constant is zero, then with a step change in the input to a definite value such that $x = x_s$ = constant, and according to equation (I-6), we have $y = 0$. It is only at the instant of a step change in x, that is, at the time origin $\tau = 0$ that the derivative $dx/d\tau = \infty$, and the response takes the form of an instantaneous impulse, that is, the output varies from zero to infinity and goes back to zero (Fig. I-7*c*).

It should be noted that in real elements the output cannot change instantaneously: because of the time lag it will always change over a period of time (see page 30). With allowance for time lag, the equation of a differentiating element takes the form:

$$y = (Kx_s/T)\, e^{-\tau/T} \tag{I-7}$$

At $T = 0$ (a pure differentiating element) the response (Fig. I-7*d*) described by Eq. (I-7) reduces to an impulse response (Fig. I-7*c*).

An integrating element. This type of element is also called astatic or neutral. For such an element, the response to a step change in the input is the integral of the excitation (the ramp response):

$$y = \frac{1}{T}\int_0^{\tau} x d\tau \tag{I-8}$$

At $x = x_s$ = constant

$$y = \frac{1}{T} x_s \tau \tag{I-8a}$$

A $y-\tau$ plot of Eq. (I-8*a*) yields a straight line going from the origin of coordinates (Fig. I-7*e*).

A pure delay element. This type of element is also called a distance-velocity lag element, thereby indicating that because of the finite rate of flow of the material, a change in the input variable will not appear at the output of the element until a certain time has elapsed. For this type of element, a step change in the input variable shifts the response by a time equal to τ_d:

$$y(\tau) = x(\tau - \tau_d) \tag{I-9}$$

A pure delay element is identified with the so-called plug-flow model (see page 109).

An oscillatory element. In this type of element, when the input signal is altered suddenly, the output signal, as it approaches a new steady-state value y_s, oscillates about it with an amplitude decaying exponentially (the dashed lines in Fig. I-7*f*):

$$y = y_s\left[1 - e^{-\tau/T}\left(\cos \omega\tau + \frac{1}{T\omega} \sin \omega\tau\right)\right] \tag{I-10}$$

where T is the time constant of damped oscillations and ω is the frequency of oscillations.

Noise. In real systems, signals carrying information never come through in pure form, but are distorted by random disturbances, or noise that is always present in communication channels.

As often as not, a chemical process fails to be reproducible: that is, it takes a new path every time it is realized. This happens because of a high noise level in chemical processes. The detection of useful signals embedded in noise is a key objective of the analysis and synthesis of chemical-engineering processes.

The efficiency of a given system in data transmission by signals, or communication efficiency, depends on the operating principle, system configuration, system instrumentation, and the types of signal used. Since all practical communication channels are subject to noise, communication theory uses the concept of the *average signal-to-noise power ratio*, H_s, defined as the logarithm to base 2 of the ratio of the signal power, P_s, to the noise power, P_n, at the system output, that is,

$$H_s = \log_2 P_s/P_n \tag{I-11}$$

Besides, a signal is characterized by *duration* T_s and *bandwidth* Δf_s, A generalized characteristic of a signal is its *information capacity*, V_s· defined as:

$$V_s = H_s T_s \Delta f_s \tag{I-12}$$

The capacity of a communication channel to store or communicate information is defined by the product

$$V_c = H_c T_c \Delta f_c \tag{I-13}$$

where H_c is the logarithm of the power range, T_c is the transmission time of the channel, and Δf_c is the bandwidth of the channel.

If a channel is to transmit a signal without distortion, it is essential that $V_c \geqslant V_s$. As the ratio V_c/V_s increases, the transmission reliability and the noise immunity of the channel improves, but its efficiency is decreased. Transmission reliability and noise immunity increase exponentially with an increase in the so-called *redundancy* defined by the expression

$$j = \left(1 - \frac{1}{V_c/V_s}\right) \tag{I-14}$$

By holding the ratio V_c/V_s constant, we may trade a decrease in bandwidth for an increase in power range or an increase in transmission time, etc.

When we analyse or describe mathematically various processes of chemical engineering, we usually run into two broad classes of processes, *discrete* and *continuous*. Accordingly, these events are sources of discrete and continuous information.

Discrete processes comprise individual events whose number may be finite or infinite, but always representable by numbers. This statement applies to the structure of matter, the energy levels of electrons in atoms, light, electric current as a flow of charged particles, and the like. Operation of reactors in chemical-engineering systems may likewise fall under this heading.

Components that mechanize discrete processes (say, switches) may have a finite number of states. A transition from one state to another occurs stepwise, and for each transition there are two positions of the device; one is the ON position (with the signal passing through) and the other is the OFF position (the signal passage is blocked).

Continuous events fill the time interval under observation (finite or infinite) so that we cannot single out and number them separately.

Sometimes, discrete processes may change into continuous ones. In fact, a continuous process may be looked upon as the limit to which a discrete process will tend if the time (or spatial) separation between the constituent events tends to zero. Conversely, a discrete process may be treated as a continuous one observed at finite intervals.

As regards signals, they may show an amplitude continuity, a time continuity, or both. The amplitude continuity may be removed by amplitude quantization, or simply *quantizing*. The time continuity may be removed by

sampling. In some cases, the original signal waveform may be both quantized and sampled.

With quantizing, the output is a waveform whose amplitude values are selected from a discrete set, but whose jumps from one value to another occur at arbitrary times.

With sampling, the original signal waveform is observed periodically at fixed sampling intervals, and a sequence of sample values is derived from the continuous time function.

A waveform which has been both sampled and quantized produces a sequence of sample values each of which has been selected from a discrete set, closest to the true values of the continuous signal waveform. This combination of sampling and quantizing is equivalent to presenting a signal by a sequence of numbers and transmitting them at fixed instants of time.

In 1933, V. Kotelnikov of the Soviet Union came out with his sampling theorem* which states [6] that if a continuous waveform is band-limited to frequencies between 0 and f_{max}, then it can faithfully be represented by its samples taken at a sampling interval

$$\Delta\tau = 1/(2f_{max}) \quad \text{(seconds)} \tag{I-15}$$

I-4. BASIC CONCEPTS AND DEFINITIONS OF CONTROL THEORY

Feedback. The concept of feedback is fundamental in cybernetics as the basis of automatic action in both nature and engineering systems. It may be defined as the reflection of a process upon its own action.

Feedback is an attribute of closed-loop systems in which it may have any one of two effects. If feedback accelerates or builds up a process, we speak of *positive feedback* (an example of positive feedback is provided by chain reactions). If, on the other hand, feedback tends to slow down a process, we have *negative feedback* (an example is provided by the combustion of coal in a closed space).

In engineering systems, feedback is utilized to control processes, for which purpose the signal from the system output is used to act upon the input. An example is offered by the negative feedback system illustrated in Fig. I-2. The controller continually follows the output variable of the controlled process and compares it with the desired value (set point) of the measured variable stored in the controller as a set-point adjustment. If there is a difference between the two values, the controller generates an error signal which is used as the actuating signal for the final control element (the control valve), and the final control element adjusts the flow of energy or material entering or leaving the process, thereby forcing the error to zero, so that the measured variable is restored to its set point.

* It is known as the Shannon theorem in the American and British literature — Tr.

Feedback systems may be with or without a time lag. In the former, changes in the controlled condition will not show up until after some time (for example, there may be a time delay in the effect of heat build-up on the composition of the end product). This time lag, or a gradual change in the output variable following a sudden change in the input variable, is a specific feature of chemical systems. This is why time lag compensation and use of anticipatory (or preact) control figure prominently in the science and art of automatic control in chemical processing.

Transient response. In order to establish what the control system is to do and how, the process is analysed dynamically and its model is constructed along the general lines shown in Fig. I-5. The mathematical model then serves as a basis for a block diagram of the control system, and finally automatic control components, or hardware, are selected to fulfil the functions assigned to the control system. Because of the extreme complexity of chemical-engineering processes, however, their dynamic models are unwieldy and difficult to instrument. This is the reason why the more recent trend has been to design automatic control systems on the basis of experimental data gathered directly on the process or plant in question.

The controllability of a plant or process is established by watching a test signal through the plant and analysing the responses (the stimulus-response technique or response analysis testing). In control theory, resort is usually made to transient response to a step input. The term "transient" implies that a sudden change in input causes the process to change from one steady state to another.

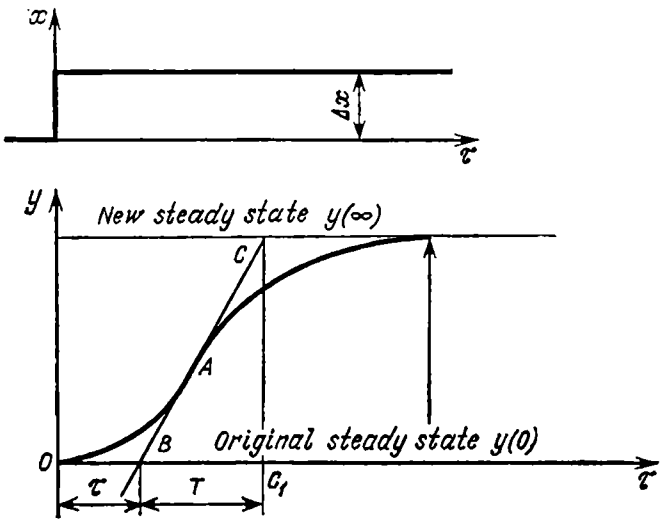


Fig. I-8. Delay time, time constant and gain of a process

The following characteristics related to the controllability of a process can be derived from its transient response curves: delay time, time constant, and gain (Fig. I-8).

Delay time. Draw a straight line, *BC*, tangent to the transient response curve at the point where the slope is a maximum (point *A* in Fig. I-8), and

extend it until it intersects the line representing the previous steady-state value (point B). Then the time interval from the initiation of the step input to the instant represented by the intersection of the tangent line and the time axis (intercept OB) will give the total *delay time*, τ, of the system. The total delay time, τ, is the sum of the pure delay (distance-velocity lag) and the capacitance delay. In solving practical problems, use is ordinarily made of this total delay time, τ.

Time constant. The time-axis intercept between the points where the line tangent to the response curve intersects the previous steady-state line and the new steady-state line (intercept BC_1 in Fig. I-8) is called the *time constant*, T, of the system. The time constant is a time interval over which the output variable would change from its initial to a new steady-state value, if this change occurred at a constant and maximum rate under given transient conditions. In chemical engineering, the time constant T usually represents the ratio of the reactor hold-up, V m^3 to the throughput, or the volume of fluid, in m^3, passed through the reactor every second, V_q, that is,

$$[T] = [V/V_q] = [\mathrm{m}^3 \times \mathrm{m}^{-3} \times \mathrm{s}] = [\mathrm{s}]$$

Thus, the time constant of a system describes its ability to accumulate or dissipate a material or energy. The greater the time constant of a system, the greater its delay time, and the more sluggish is its response to control action.

As already noted, a considerable delay time occurs in chemical-engineering systems, and their time constant runs into many seconds, minutes, or even hours. It is customary to evaluate the sluggishness in terms of a dimensionless parameter, τ/T.

Single-capacitance and multi-capacitance systems. As stems from the concept of time constant, the sluggishness of a system is directly related to its capacitance. The greater the capacitance of a reactor, the lower the rate at which the process variables change, all other conditions being equal.

The capacitance of a system may be constant or variable. If the diameter of a liquid-filled tank remains the same with height, the reactor capacitance will be constant. If, on the other hand, the reactor diameter varies with height, its capacitance will be variable, too. In heat exchangers and similar units, the capacitance may be variable because of changes in the specific heat of the liquid.

Chemical-processing systems may be divided into single-capacitance and multi-capacitance.

The term "single-capacitance" applies to all tanks and reactors with a controlled liquid level, reactors in which the temperature is controlled by mixing two liquids (or a vapour and a liquid), pipelines with a controlled flow rate or pressure, plants in which vapour or gas pressure is controlled.

A multi-capacitance system may have two, three or more tanks and is, in effect, a series chain of several single-capacitance elements.

An example of a two-capacitance system is provided by a jacketed heat exchanger which consists of the thermal capacitance of the jacket and the thermal capacitance of the medium. Strictly speaking, this is not a two-

capacitance system because the wall between the two capacitances is a third capacitance also accumulating heat. Since, however, the wall is thin and its material has a very high thermal conductivity, this capacitance may be neglected and lumped with any one of the two capacitances. If the wall had a considerable mass capable of accumulating a relatively large amount of heat, the system would be one having three capacitances.

The gain of a system is the ratio of a change in its output variable to the unit change in the input variable that caused it as the system goes over from the initial state to a new steady state.[9]

In control practice, the unit step disturbance is usually taken to be the ratio of the unit flow rate of the manipulated medium to per cent of the final control element travel.

Thus, the gain of a controlled system, as derived from its transient response curve is defined as (see Fig. I-8)

$$K_s = \frac{y(\infty) - y(0)}{\Delta x} = \frac{\text{unit of output variable}}{\text{per cent of final control travel}} \tag{I-16}$$

where $y(0)$ is the output variable in the initial steady state; $y(\infty)$ is the output variable in the new steady state; Δx is the input disturbance expressed as the percentage of the final control travel.

Instead of gain, a controlled system may be described in terms of its self-regulation factor.

The *self-regulation factor* of a controlled system is defined as the reciprocal of its gain, that is, as the ratio of a change in the input variable to the resultant change in the output variable. As a rule, the input variable is expressed in terms of its ratio to the total travel of the final control element or the total flow of the manipulated medium, and the output variable is expressed in terms of its ratio to the maximum set-point value obtainable under given operating conditions.

Thus, the self-regulation factor may be described by an expression of the form

$$\rho = \frac{\Delta x y_s}{[y(\infty) - y(0)] \times 100} \% \tag{I-17}$$

where y_s is the set-point value of the output.

Static and astatic systems. Depending on the manner in which the output signal varies, all systems may be classed into static and astatic.

A *static system* is that in which the output variable takes on a new steady-state value after a disturbance ceases. Another name is a *self-regulating system.*

An *astatic system* is that in which the output variable fails to reach a new steady state after a disturbance is removed. Another name is a *nonself-regulating system.*

Determination of dynamic characteristics. In designing a control system, it is customary to take several measurements of τ, T and K_s under the same load conditions and to determine their arithmetic means, τ_m, T_m, and $K_{s,m}$.

As a measure of the tendency for the results to disperse, standard deviation is found for each quantity. Thus, for the delay time the standard deviation is

$$s_\tau = \sqrt{\frac{\sum (\tau - \tau_m)^2}{n}} \qquad \text{(I-18)}$$

where n is the number of observations.

For the other quantities, T and K_s, the standard deviation is found in a similar manner.

The number of observations, n, that should be made in order to keep the arithmetic means of τ, T and K_s within the acceptable limits is given by Eq. (I-18).

The next step is to compare the observations made under various load conditions, with τ/T limited to its average value over the entire range of changes in load, while the value of $K_{s,m}$ is chosen to be a maximum just short of causing an oscillatory response to control action.

Controlled and manipulated variables. After the dynamic characteristics have been found, the next step is to define *controlled variables*. These are output variables most representative of the system. Among other things, they should give a measure of the throughput of the system, the quality of the end product, and the economy of the process. Controlled variables may be either physico-chemical quantities measured directly, or indices continually and automatically inferred from several observations.

In feedback systems, *manipulated variables* are usually some of the input variables. The manipulated variable (or variables) is changed so as to compensate for any deviations of the process from the desired path and to cause the controlled variable to move towards the set point.

As already noted, the delay time τ, the time constant T and the gain factor K_s are found for the main input-output loops of a process. The $x-y$ loop for which K_s is relatively high while τ and T are low is usually chosen for the manipulated variable.

If several loops of a system have comparable values of τ, T and K_s, the system is multivariable. To simplify analysis, it may be treated as one consisting of an appropriate number of independent single-variable subsystems. This approach is only valid in cases where each manipulated variable affects only one controlled or output variable. Otherwise, inter-loop relationships will have to be allowed for.

Control action. Once the controlled and manipulated variables are defined, the designer is in a position to move on to the selection of a particular *control action* and, accordingly, of a particular controller type and controller settings.

A control action is usually described by a *controller equation* which relates the deviation of the controlled variable from the set point, y (which is the input for the controller and the output for the process) to the displacement of the associated final control element, x (which is the controller output and the process input) in the time domain.

In different controllers, a control action is applied differently, using feedforward or feedback, or both.

With a given control action, operation of a controller is also decided by the values of the parameters entering the respective controller equation (controller settings). The settings of commercial controllers may be adjusted between wide limits, so that a controller may be tuned to respond to a fairly wide range of changes in the dynamic characteristics of the controlled system.

I-5. MAIN TYPES OF CONTROLLERS

The currently available commercial controllers may be classed into continuous and periodic types.

In a *continuous-action controller*, a continuous functional relationship is maintained between the input and output. Continuous-action controllers are usually applied to individual unit processes.

A *periodic controller* monitors the controlled variable periodically (at discrete time intervals) and generates an output as a sequence of pulses whose amplitude, duration and/or frequency are functions of the input signal at each sensing instant. Periodic controllers are usually applied to a combination of several unit processes.

The most common control actions and the respective controllers are examined below.

According to control action, all continuous-action controllers may be divided into four types as follows: proportional (or P-) controllers, integral (or I-) controllers, proportional-integral (or PI-) controllers, and proportional-integral-derivative (or PID-) controllers.

The control action of a *P-controller* is described by the equation

$$x = K_C y \tag{I-19}$$

where x is the controller output (the position of the associated final control element), y is the controller input (the deviation of the controlled variable from the set-point, or the error signal), and K_C is the proportional gain. The controller setting is changed by adjustment of K_C.

The control action of an *I-controller* is described by the equation

$$x = K_{C1} \int y \, d\tau \tag{I-20}$$

where K_{C1} is the integral gain factor which describes the speed with which the associated control element operates in response to a given change in the error, y. This type of controller is set by adjustment of its integral gain, K_{C1}.

Combining proportional and integral actions produces a *PI-controller* whose action is described by an equation which is the sum of the respective equations for P- and I-controllers

$$x = K_C y + K_{C1} \int y \, d\tau = K_C \left(y + \frac{1}{T_R} \int y \, d\tau \right) \tag{I-21}$$

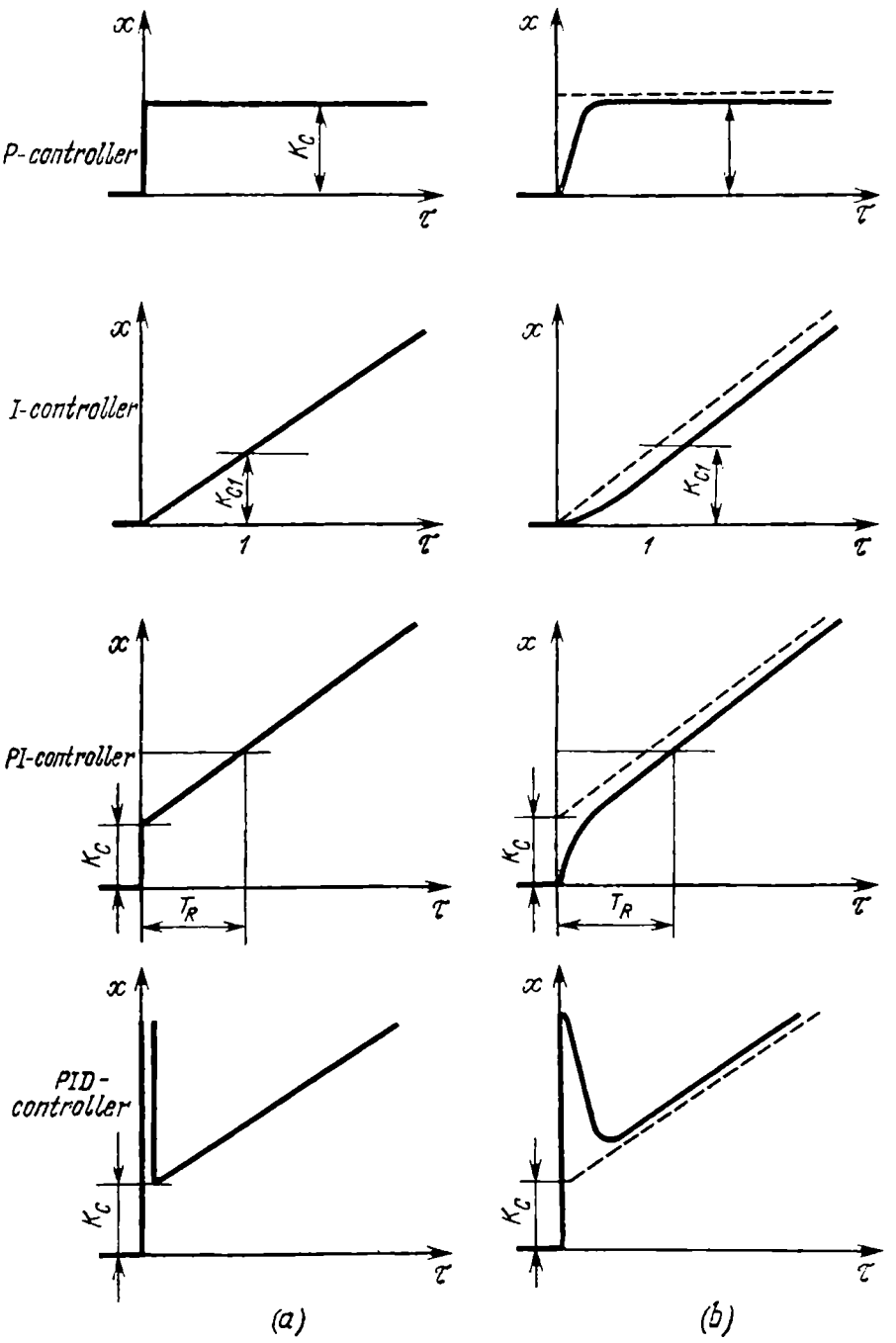


Fig. I-9. Transient responses of standard controllers
(*a*) idealized controllers; (*b*) real controllers

where T_R is the reset time. This type of controller is set by adjustment of its proportional gain factor K_C and its reset time T_R.

The control action of a *PID-controller* is a combination of proportional-integral action and derivative or rate action (sometimes called anticipatory or preact action):

$$x = K_C y + K_{C1} \int y \, d\tau + K_{C2} \frac{dy}{d\tau} = K_C \left(y + \frac{1}{T_R} \int y \, d\tau + T_D \frac{dy}{d\tau} \right) \quad \text{(I-22)}$$

where K_{C2} is the derivative gain factor and $T_D = K_{C2}/K_C$ is the derivative or rate time. This type of controller is tuned by adjustment of its gain K_C, its reset time T_R and its derivative time T_D.

The step function responses of the above controllers according to Eqs. (I-19) through (I-22) and of commercial controllers appear in Fig. I-9.[10]

The main points to be borne in mind when selecting a particular type of controller are the maximum deviation of controlled variables from their set-points (the error range), settling time, the offset (the residual difference between the final and original values of the controlled variable), and the limits of overshoot. A specific make of controller and the form of energy for its operation are selected according to service conditions and the choice available commercially.

After a controller has been selected, the equations describing the controlled process and the controller are solved simultaneously.

A simultaneous solution of these equations, with allowance for the disturbances acting on the process, leads to a closed-loop control system. The solution is usually obtained by simulation (mathematical modeling) on analog computers. With analog computers, the parameters of the system elements (the properties of the process and controller settings) can readily be changed to trace their effects on the behaviour of the system as a whole.

The optimality of control can be evaluated on the basis of the parameters discussed above. Alternative criteria of the "quality" of control may be the time integral of the error squared, $\int y^2 \, d\tau$, or the time integral of the error, $\int y(\tau) \, d\tau$. Control is optimal if these integrals have a minimum value.

I-6. INFORMATIONAL CHARACTERISTICS OF INSTRUMENTS FOR INDUSTRIAL CONTROL

At present, a vital and urgent problem facing engineering cybernetics is to utilize information theory in order to derive qualitative criteria for industrial control components, criteria that would form a scientific basis for the design, standardization, calibration and use of instruments.

A brief outline[11, 12] of the criteria that might be used to obtain the informational characteristics of the most common instruments follows.

Basic definition. One of the basic informational characteristics is the information *capacity of an instrument*, that is, the maximum rate at which

a given instrument can measure, convert or register information, or the amount of information that this instrument can generate per unit time.

As the first step, we shall discuss a series chain of two information elements with capacities C_1 and C_2. The capacity of the chain will then be C_c.

Let us call the ratio of the capacities of two successive elements the *match factor*, K'. Then

$$K' = C_2/C_1 \tag{I-23}$$

Three cases are possible with the match factor, namely:

(a) the ideal compatibility case, where $C_2 = C_1$ and $K' = 1$. The capacity of the chain will be determined by any element: $C_c = C_1$ and $C_c = C_2$;

(b) the redundancy case where $C_2 > C_1$ and $K' > 1$. The capacity of the chain will be limited by C_1, and $C_c = C_1$;

(c) the filtering case where $C_2 < C_1$ and $K' < 1$. Then C_c will be limited by the capacity of the second element, $C_c = C_2$.

According to the final goal sought, the above chain may consist of the measuring and indicating parts of an instrument, or a data transmitter (sensor) and a data receiver (indicator). This approach is convenient where an information chain consists of a large number of elements.

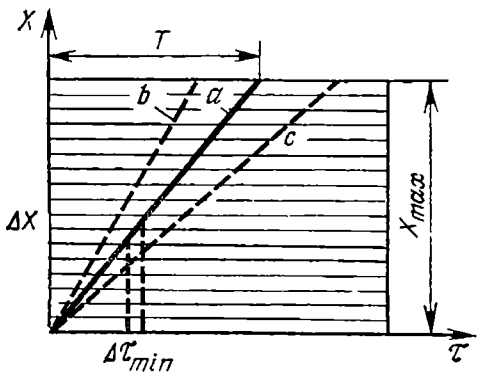


Fig. I-10. Scale of a measuring instrument
ΔX — quantizing interval

Capacity of a measuring element. Commercially available instruments are divided into accuracy classes. An accuracy class is a number which specifies the instrument's limits of error, ξ, expressed in per cent of the full-scale value (reading or deflection), usually abbreviated to f.s.d., or the scale range. It may be assumed that the error is uniformly distributed over the range $\pm\xi$.

An attempt to measure a physical quantity to an accuracy better than the limit of error, $|\xi|$, of a given instrument has no sense. Accordingly the scale (or range) of an instrument may be quantized, that is divided into intervals, without loss of information (Fig. I-10), according to the equation

$$\Delta X = (2\xi/100)(X_{\max} - X_{\min}) \tag{I-24}$$

where $X_{\max}$ and $X_{\min}$ are the maximum and minimum values of the quantity being measured.

Then the number of quantizing steps will be given by

$$N = (X_{\max} - X_{\min})/\Delta X \tag{I-25}$$

Solving Eqs. (I-24) and (I-25) simultaneously, we get

$$N = 50/\xi \tag{I-25a}$$

Here and elsewhere, ξ is a dimensionless quantity.

It may be assumed that in the course of measurement the value of the quantity being measured has an equal probability to occur in any quantizing interval, ΔX_i during the time T (where T is the time constant of the instrument or, in the case of electronic potentiometers and bridges, the time of the carriage's travel across the scale). Then the entropy of the instrument scale (or range) will be

$$H(X) = -\log_2 P = \log_2 N \tag{I-26}$$

where $P = 1/N$ is the probability associated with each interval.

Substituting the value of N from Eq. (I-25*a*) into Eq. (I-26), we obtain

$$H(X) = \log_2 (50/\xi) \tag{I-27}$$

Referring to Fig. I-10, the line *a* uniquely defines the value of T, because the line *b* exceeds the speed of response of the instrument, while the line *c* falls short of its dynamic capability. Thus, the capacity of the measuring element of an instrument can be described by the equation

$$C_m = H(X)/T \tag{I-28}$$

or, noting Eq. (I-27)

$$C_m = \frac{\log_2 (50/\xi)}{T} \tag{I-28a}$$

If the values of ξ and T are specified in advance, the last expression may be used in the design of instruments satisfying appropriate instrumental requirements. From the function $C_m = f(\xi, T)$ it is seen that accurate but slow measurements carry as much information as less accurate but faster measurements.

A major advantage of the informational characteristics of instruments is that they embrace both the dynamics and accuracy of instruments. Besides, knowing the value of C for each element, one can derive an optimum configuration for a system intended for the acquisition and reduction of mass information.

The values of C_m for some stock-produced instruments are given in Table *I-1*.

As is seen from the table, the chain made up of a ГИП-5 gas-analyzer sensor and an ЭПД-02 potentiometer will be redundant, because $K' = 0.433 \div 0.058 = 7.6$

Records. The information generated by instruments is recorded and stored on circular or strip charts ruled in appropriate units (or percentages) in a form convenient for subsequent use. However, ease of readout depends on the quality of records—with poor records the loss of some information may be irrecoverable. In turn, the quality of records depends on a proper match between the rate at which it is generated, or the capacity of the measuring element, C_m, and the rate at which it is recorded, or the capacity of the recording element, C_r.

It has been noted that the measuring and recording elements of an instrument are two series elements of an information-handling chain. We have already

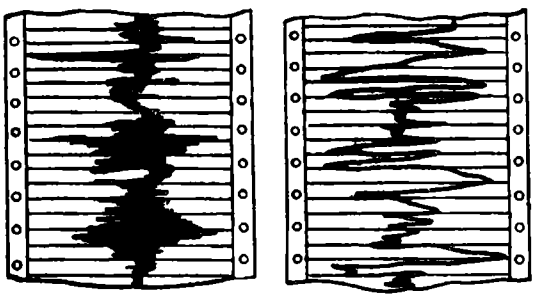
Table I-1

Instrument	Accuracy class, ξ	Time constant, T, s	Capacity, C_m, bits/s
Automatic electronic potentiometers and circular-chart bridges:			
ЭПД-02 and ЭМД-102	0.5 (0.5)*	15 (5)*	0.443 (1.329)*
ЭП-102 and ЭМ-120	0.5	20	0.332
ЭПП-09 and ЭМП-109	0.5	8	0.830 (0.353)**
	0.5	2.5	2.657 (1.129)**
	0.5	1	6.644 (2.822)**
Electronic balanced-bridge recorders:			
КВ/Т and КВ/W	0.5	1.5	4.429
Electronic differential-transformer recorder, ЭПИД	1.0	15	0.376
Ferrodynamic instrument, ВФ	0.5	20	0.332
Diaphragm differential manometer, ДМК-Р	1.0	2	2.822
Secondary recorder, 1РЛ-29А	1.0	0.5	11.288
Pneumatic compensated differential pressure gauge, ДМПК-4	1.0	1	5.644
Float-type differential pressure gauge, ДП-280 for 33,330.5 N/m^2	1.5	4	1.261
Draft gauge, ТНСК	2.5	25	0.173
Gas analyzer sensor, ГИП-5	10.0	40	0.058
Thermal-conductivity gas analyzer, ТКГ-5	5.0	180	0.018

* The values of ξ, T, and C_m in brackets apply to fast-rate operation.
** The values of C_m in brackets apply to narrow-range ЭПП-09 potentiometers for which $\xi = 1$.

found the capacity of the former, C_m. Now we shall determine that of the latter, C_r.

Example I-3. A single-point ЭПП-09 potentiometric recorder produces a record on a strip chart. The chart is advanced at a rate of $v = 60$ mm/h; the traversal time T is 8 s; the record width is $b = 0.5$ mm.



(*a*) (*b*)

Fig. I-11. Records on a strip chart
(*a*) $v = 60$ mm/h; (*b*) $= 240$ mm/h

Under the circumstances, the capacity C_r is less than the value of C_m given in Table I-1 ($C_r < C_m$, the filtering case) and, as stems from Shannon's theorem,[8] a loss of information is inevitable. In our example, this loss takes the form of record traces superimposed on one another,

as is shown in Fig. I-11. Practically, records can be discerned if there are not more than two trace widths to the millimetre of chart width. Simple calculation shows that chart *a* will contain 7.5 trace widths.

The record capacity C_r is different for each chart speed and is given by

$$C_r = K'C_m \tag{I-29}$$

The match factor may be assumed to be

$$K' = \alpha Tv/b \times 3600 \tag{I-30}$$

where α is the ratio of the range of changes in the measured variable to the scale (or range in use). In practice, $\alpha = {}^1/_3$.

Substituting the numerical values in Eqs. (I-28) and (I-29), we obtain

$$K' = \frac{8 \times 60}{3 \times 0.5 \times 3600} = 0.089$$

$$C_r = 0.89 \times 0.83 = 0.074 \text{ bits/s}$$

From Eq. (I-30), one can readily find the optimal speed v_{opt} at which $C_r/C_m = K' = 1$ (at $K' > 1$, some of chart length will be wasted, and at $K' < 1$, a loss of information will occur):

$$v_{opt} = \frac{b \times 3600}{\alpha T}$$

For circular-chart instruments the relationship between the measuring and recording elements is less favourable. Because of the low rotational speed of the chart and the difference in time scale along the radius, r, the recording speed, $v = \varphi(r)$, for such instruments

$$C_r = K_1' K_2' C_m \tag{I-31}$$

The factor K_1' can be found from Eq. (I-30), on the condition that $v = 2\pi R/24$. The factor K_2' is given by

$$K_2' = \frac{R + r_0}{2R} \tag{I-32}$$

where r_0 and R are the radii at the beginning and end of the circular chart (in mm).

The quantity K_2' takes care of the information lost because of variations in recording speed with radius. For Type ЭПД-02 and ЭМД-102 recorders for which $R = 133$ mm and $r_0 = 28$ mm, we have $v = 35$ mm/h and $K_2' = 0.6$. It is interesting to note that the high-rate operation of these recorders (the f.s.d. time is $T = 5$ s) does not increase the capacity of the instrument ($C_{instr} = C_r$) which is in fact independent of time T. This can readily be ascertained by substituting the respective values from Eqs. (I-28*a*) and (I-30) for K_1' and C_m in Eq. (I-31) at $\alpha = 1$:

$$C_{instr} = \frac{K_2' v}{b \times 3600} \log_2 (50/\xi) \tag{I-33}$$

Here, the record error is $\xi = 1$.

For the circular-chart recorders cited above, $C_r = C_{instr} = 0.067$ bit/s and $C_m = 1.329$ bits/s. Thus, $C_r/C_m = 0.05$. In other words, the information-handling capacity of the recording element in Type ЭПД and ЭМД instruments is only 5% of the capabilities embodied in their design. These instruments are still used only because the amount of information applied to their inputs is in most cases only a fraction of their capacity.

In such cases, it is legitimate to question the match between the measured process and the measuring system. Besides, in cases calling for human intervention, use is only made of the information directly related to the deviation of the controlled variable from the set-point value; the remainder, usually occupying a greater part of the chart, is actually superfluous.

I-7. CONTROL METHODS AND CONTROL SYSTEMS

From the foregoing it is seen that the concept of control covers a variety of control actions over input variables performed for the purpose of securing the desired output from a system. These forms of control and, as a consequence, the systems that accomplish them can be classed according to the objective sought.

Functionally, automatic control systems may be of any one of the following types.

Regulator operation. With regulator operation, the objective is to have the output variable remain at the set-point value in spite of changes in load variables:

$$\hat{y} - y \to 0 \tag{I-34}$$

where $\hat{y}$ is the set-point value of the output variable and y is its current value.

The two values are related as

$$\hat{y} - y = e_y \tag{I-35}$$

where e_y is the error signal.

The controller operates on the error and produces a signal which actuates the associated final control element, usually a control valve. The control valve brings about appropriate changes in a manipulated variable, and this tends to move the controlled or output variable towards its set-point value.

Servo operation. With servo operation, the set-point value of the output variable, $\hat{y}(\tau)$, is changed with time in an arbitrary manner, say, according to the changing requirements of the operator.

Programmed control. With programmed control, changes in $\hat{y}(\tau)$ are made to follow a predetermined program.

Optimal control. With this control, the objective is to search for an optimum transition from one steady-state condition to another.

Extremal control. With this form of control, optimum conditions for a process cannot be specified in advance, and a special control mechanism

searches for an extremum (maximum or minimum) of some process variable (the optimization criterion), and the system then maintains it.

Adaptive control. In this form of control, the system searches for and implements optimum process conditions in the face of changes in process parameters.

All of these forms of control may be subject to constraints related to error compensation. These constraints may require that (a) the error signal be kept to a minimum; (b) the error signal be minimized as rapidly as practicable; or (c) the error signal be always of the same sign, that is, there should be no hunting. A good control system is usually a compromise between the first two constraints, that is, between a small error signal and a fast response.

The above listed forms of control can be realized by any one of two methods or schemes, namely the *open-loop scheme* and the *closed-loop scheme.*

For simplicity, we shall examine each scheme, using linear systems as examples. A linear system is that in which the inputs and outputs of the constituent elements are related by linear differential equations. These equations are simple to analyse, and the results are applicable to many practically important problems.

The state of a linear system may conveniently be described in terms of its transfer function, G. When written in operator notation, the system transfer function makes it possible to describe the relations between its constituent elements by simple equations (p. 106).

The transfer function connects the output variable y to the input variable x by an equation of the form

$$y = G_n(x)$$

where n is the number of states of the system.

Then the constituent elements of the system with transfer functions $G_1, G_2, G_3, \ldots, G_n$, connected in series or in parallel, may be represented by a single element with a transfer function

$$G = \bar{y}/\bar{x} \tag{I-36}$$

where $\bar{y}$ and $\bar{x}$ are the transforms of the respective variables.

For elements connected in series, the overall transfer function G is equal to the product of the individual transfer functions:

$$\bar{y}/\bar{x} = G = G_1G_2G_3 \ldots G_m \tag{I-37}$$

and for elements connected in parallel, the overall transfer function is the sum of the individual transfer functions

$$\bar{y}/\bar{x} = G = G_1+G_2+G_3+ \ldots +G_m \tag{I-37a}$$

If we assume that the desired (set-point) output variable, $\hat{y}$, is secured by at least one change in the manipulated input, $\hat{x}$, the system may be compensated for deviations from the set-point, and the output variable is given by

$$\hat{y} = G\hat{x} \tag{I-38}$$

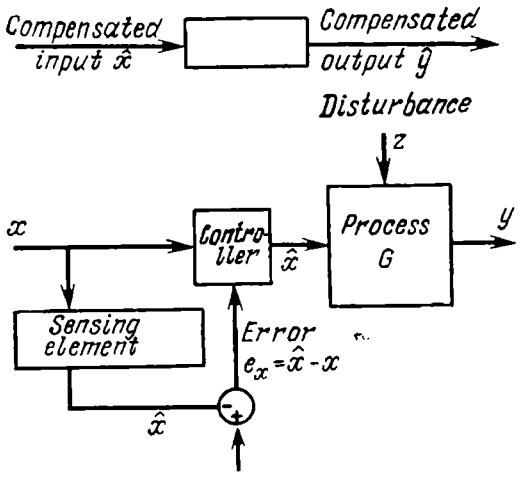


Fig. I-12. Open-loop system (a compensated system at top of the figure)

Such a system may be depicted by a block-diagram such as is shown at the top of Fig. I-12.

Open-loop control. An open-loop control system may be constructed by two methods (Fig. I-12). Using the error compensation principle one may construct an open-loop system such as is shown in Fig. I-12. In this scheme, the input variable may be adjusted to compensate for the expected error, $e_x = \hat{x} - x$, and the regulator then maintains the input variables x at the level $\hat{x}$.

However, the disturbances, z, acting on the process cause the output variable y to deviate from its set-point value, $\hat{y}$, thereby producing an error. Since $\hat{x}$ is maintained constant irrespective of disturbances, the following relationships exist between the disturbance z and the error in y. On the basis of Eqs. (I-34) through (I-36), we have

$$e_y = (\hat{y} - y) = G(\hat{x}) - y \tag{I-39}$$

Referring to Fig. I-12,

$$y = G(\hat{x}) + G'(z) \tag{I-40}$$

whence

$$e_y = G'(z) \tag{I-41}$$

where $G'(z)$ describes the effect of the unknown and uncontrollable disturbance on the output process variable.

Examples of open-loop systems are provided by processes controlled by appropriate changes in some characteristics (say, moisture content) of the source material; as a result, the output variable is kept within the desired limits.

Feedforward control. The vulnerability of the open-loop method to disturbances suggests constraining the disturbances so that they will not enter the process or correcting for them in the system. If we know in advance that the quality of a raw material is subject to changes (disturbances), we have two alternatives before us:

(a) either to use various blends of the raw material from a stock-pile so as to keep the feed composition constant;

(b) or to tolerate variations in the quality of the raw material as inevitable and to compensate for them through changes in the process settings.

In each case, one has to rely on one's past experience. Thus feedforward control cannot be realized without some knowledge of the process's history.

In block-diagram form, a process under feedforward control is shown in Fig. I-13. The deviations in the input and output variables from their set-points can be described by the following equations

$$e_x = (\hat{x} - x)$$

$$e_y = (\hat{y} - y)$$

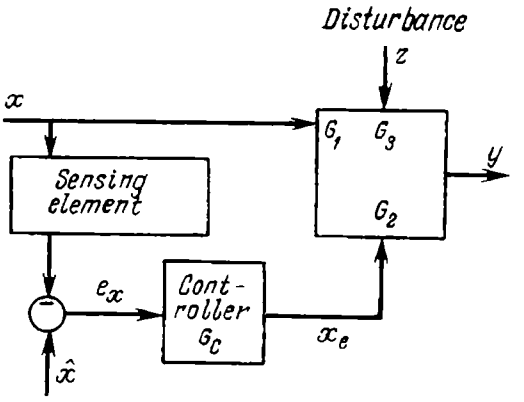


Fig. I-13. Block-diagram of a feedforward control system

In the case of zero deviations, that is, at $x = \hat{x}$, $\hat{y} = G_1\hat{x}$. Referring to Fig. I-13, the output variable may be regarded as an outcome of three effects, namely G_1 operating on x, G_2 on x_e, and G_3 on z. Then, according to Eq. (I-37*a*)

$$y = G_1x + G_2x_e + G_3z \tag{I-42}$$

where x_e is the output of the controller G_C defined as

$$x_e = G_Ce_x \tag{I-43}$$

From Eqs. (I-38), (I-42) and (I-43), we find

$$y = G_1x + G_2G_Ce_x + G_3z$$

whence

$$e_y = (G_1 - G_2G_C)e_x - G_3z \tag{I-44}$$

Thus, the conditions necessary for the disturbance to be completely compensated for are as follows:

at $z = 0$

$$(G_1 - G_2G_C) = 0 \tag{I-45}$$

$$e_y = -G_3z = 0 \tag{I-46}$$

From Eq. (I-45) it may be concluded that for an intelligent selection of a controller, G_C, one must know the effects G_1 and G_2 on the process and its input variables, that is, one must be able to predict the behaviour of the process. This is why disturbance-compensating control is employed in situations where disturbances are known and can be measured.

Thus the accuracy of feedforward control is dependent on the accuracy with which the disturbances can be predicted. It should be added that feedforward control takes no action until after an error is caused by disturbances, z [see Eq. (I-46)].

Closed-loop (feedback) control. In closed-loop (feedback) control, the output variable is utilized to act upon the system input over a feedback path in order to minimize the error.

In block-diagram form, a closed-loop or feedback control system is shown in Fig. I-14. As before and according to Eq. (I-42) for the controlled system we have

$$y = G_1x + G_2x_e + G_3z$$

With feedback, the controller output is defined as

$$x_e = G_C e_y \tag{I-47}$$

Therefore, we may write

$$e_y = \frac{G_1e_x - G_3z}{1 + G_2G_C} \tag{I-48}$$

A criterion for a feedback control system is

$$e_y \to 0 \quad \text{at} \quad G_2G_C \to \infty \tag{I-49}$$

Hence, a feedback control system offers at least two important advantages:

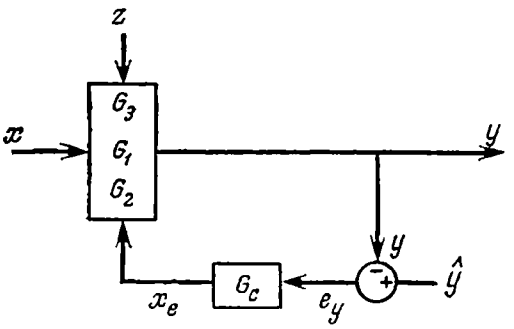


Fig. I-14. Block-diagram of a feedback control system

(1) as follows from Eq. (I-48), a feedback control system minimizes the effect of disturbances and the resultant error;

(2) as follows from Eq. (I-49), the error-minimizing criterion is the product G_2G_C which should be a substantially positive quantity.

Thus, an accurate knowledge of the process itself is not essential.

A disadvantage of feedback control is that it takes no action until after an error occurs in the process.

From Eq. (I-48) it also follows that at $1 + G_2G_C \to 0$, that is, if a negative term appears anywhere in the system, the feedback signal will be positive, and the system will oscillate, or "hunt", $e_y \to \infty$.

In some cases, it is important to know the system delay time. Otherwise, the indiscriminate use of negative feedback might cause fluctuations rather then stabilization.

A feedback control system may utilize the following control (or controller) actions (see also p. 33).

Proportional control. In the proportional control mode, the controller output is proportional to the control error (deviation from the set-point value). Therefore, Eq. (I-47) takes the form

$$x_e = K_C e_y \tag{I-47a}$$

where K_C is the proportional gain.

If the dynamics of a process are expressed in terms of constants K_1 and K_2, Eq. (I-48) may be re-cast as follows

$$e_y = \frac{K_1e_x}{1 + K_2K_C} \tag{I-48a}$$

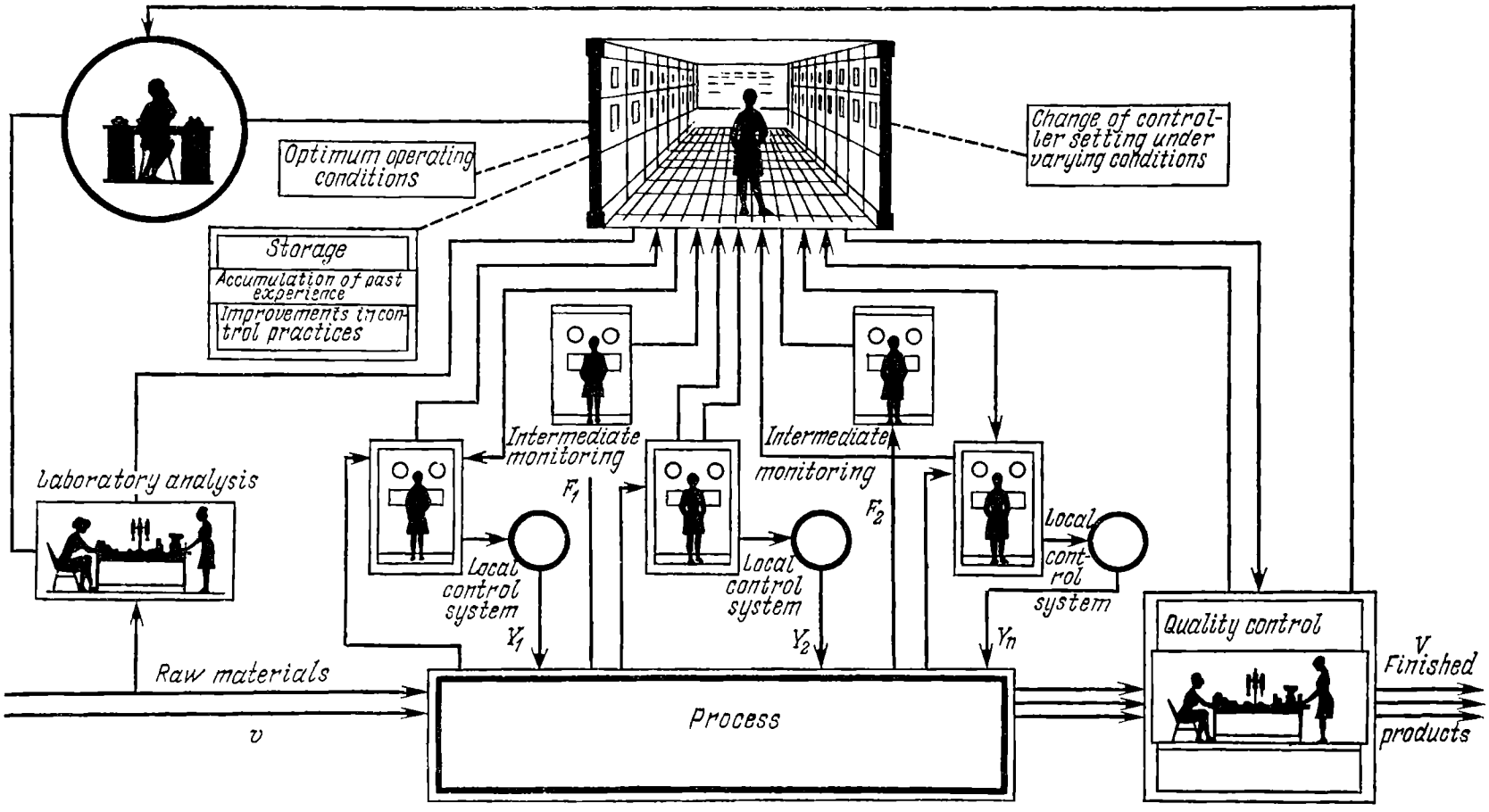


Fig. I-15. Automatic control system designed to maintain process variables

In practice, the product K_2K_C cannot be arbitrarily large. Therefore, there will always be a residual error, e_y, called the *offset*.

Integral control. The integral control mode is described by the equation

$$x_e = \frac{1}{T}\int e\,d\tau \tag{I-50}$$

The controller signal builds up as long as there is an error signal. The initial slowness of integral action can be compensated for by using a combination of proportional and integral action. This combination also does away with the offset. A measure of integral action is given by the integral time constant, T. The smaller the value of T, the faster the rate of integral control.

Derivative control. The derivative control mode is described by the following equation

$$x_e = T\,de/d\tau \tag{I-51}$$

The controller output is a maximum when the rate of change of the error is highest, but there will be no corrective action at all when the error is constant. Derivative action is beneficial for improving the stability of the system and for reducing overshoot because the correction action is fast.

As a rule, automatic control systems utilize various combinations of the control modes (or terms) described above. An automatic control system maintaining process variables on the basis of feedback and correcting for any disturbances through its own action is illustrated in Fig. I-15.

I-8. COMPUTER CONTROL OF CHEMICAL ENGINEERING SYSTEMS

So far we have dealt with what may be termed *conventional automatic control* applied mainly to maintain process variables at or near their set-points through the use of controllers appropriately tuned in advance. This form of control ordinarily applies to the lowest levels in the hierarchy of chemical manufacture, that is, to unit operations or functions (see Fig. I-3), and essentially under steady-state conditions.

As the rate of operations becomes faster and their range more complex, the need arises for manipulating the set-points in the course of the process in order to optimize the performance of the system under continually varying conditions. Under the circumstances, the human operator imposes an increasing limitation, and to ease this limitation a computer or computers are incorporated in the control loop to handle complex mathematical relationships at high computation rates.

Computer control is applied to the second and third levels in the hierarchy of chemical manufacture, that is, on a departmental or even works scale.

(A) BASIC LOGIC OF COMPUTER CONTROL IN CHEMICAL ENGINEERING

Computer process control and, especially, optimization involves a whole range of switching operations. These operations are performed in accordance with an optimum strategy formulated as a decision algorithm.[13-16]

A *decision algorithm* prescribes a number of conditions that should be satisfied in the use of physical plant under various conditions of a production cycle (start-up, shut-down, normal operation, emergency situations).

An optimum decision strategy is formulated on the basis of an analysis of the situations that are likely to develop in the use of plant under various conditions and is originally presented as a set of verbal specifications.

These verbal specifications constitute a point of departure for the synthesis of a control system that would execute the desired decision strategy. However, verbal specifications, although they are necessary, are not sufficient for a direct synthesis. Before they can serve a useful purpose, the verbal specifications must be formalized in terms suitable for computer application.

Boolean algebra. The requisite formalism has been taken over from Boolean algebra. Why has been done so will be clear from the following. Today, use of Boolean algebra for this purpose is as essential as that of, say, partial differential equations for a mathematical description of processes in a distributed-parameter system.

Boolean algebra is a mathematical system providing a convenient tool for handling logical relationships (sentences of logic) with an ease and neatness comparable to operations on algebraic symbols in elementary mathematics.

For the first time the applicability of Boolean algebra to the characterization of engineering devices was noted in connection with electric relay-contact (switching) circuits. Now it has been extended to include all applications involving the selection of decisions or strategies from among two mutually exclusive alternatives (for example, decision may be "Start the reactor", and the other, "Stop the reactor").

The need for the use of Boolean algebra in the development of decision strategies has arisen out of the extreme complexity and depth of practical control tasks and the large blocks of information involved in normal operation of control systems. Against this background, it appears worthwhile letting the reader learn some of the practical aspects in application of Boolean algebra to developing decision algorithms for chemical processes.

In this section we shall discuss the development of a decision algorithm (switching procedure) by means of Boolean algebra, taking as an example the contact reactor widely used in the chemical industry. We shall also outline the elements of Boolean algebra essential to a proper understanding of the subject-matter. For a more detailed exposition of Boolean algebra and its practical applications, the reader is referred to special texts.[13-17]

Plant switching tasks. The tasks facing a chemical-reaction engineer in his endeavour to optimize and automate his chemical process include plant switching. Plant switching is omnipresent in the chemical industry owing to

the specific character of chemical manufacture in which batch-type reactors play a prominent role.

In control of batch reactors, a well-planned decision strategy is vitally important in tackling at least three typical problems:

(1) Optimization of start-ups and shut-downs in terms of time and money.

(2) Reactor protection against failure under emergency conditions.

(3) Coordination of the various reactors discharging into a common collector (rotation of reactors for catalyst regeneration or withdrawal to a stand-by status).

Logical control. The above switching tasks are usually performed by sequential circuits which may be put in a broader category of logical control systems.

Logical control has as its goal to maintain predetermined logical relationships between signals from sensors about the state of the controlled system and the control signals applied to the final control elements (the input-output behaviour).

As with any physical system, a sequential circuit has two facets, namely: (a) an abstract facet characterized by a state or flow diagram which can analytically be presented as a system of Boolean equations and (b) a hardware facet, or the circuit realization which varies according to the type and design of components employed (these may be electronic, electromechanical, pneumatic or other bivalued devices).

Accordingly, the design of a logical control system is usually tackled in two stages as follows:

(1) Operation of the controlled system is analysed and a decision strategy is formulated.

(2) A logical machine (sequential circuit) fitting this algorithm is synthesized.

The inputs to the control logic (that is, information about the controlled process) and the output from it (control signals) have two states, one symbolized as "0" and the other as "1" (see p. 21). This binary presentation admirably fills the needs of automatic start-up, shut-down and protection, because a sequential switching circuit can execute a next-state command only after the controlled system has reached the preceding state. That the transition has taken place is unambiguously indicated by the process variables reaching certain steady-state values.

For example, before a reactor may be started up, it must be allowed an ample warm-up period. At the end of the warm-up period the reactor may be regarded as having moved from a "0" to a "1" state. The "0" state is associated with a current temperature such that $t_{cur} < t_{set}$; the "1" state is associated with a temperature such that $t_{cur} \geqslant t_{set}$.

State tables. In the above example, the reactor was assumed to have only two states, because only one bivalued or binary variable was taken to describe it. In the general case, the state of a reactor at any instant will be represented by a set of discrete values ("0" and "1") of a sufficiently great

number of bivalued variables, and these may be displayed in a single table, called a *state table*, like Table I-2 below.

Table I-2

x_1	x_2	x_3	. . . .	x_j		x_N
0	0	1	...	0	...	1
1	0	0	...	0	...	0
0	1	0	...	1	...	0
1	0	0	...	0	...	1

The rows of the table are labelled with the states that a system described by N bivalued variables can take, and the columns are labelled with the values that the input variables $x_1, x_2, x_3, \ldots, x_j, \ldots, x_N$ may take. Such a system may have (at least theoretically) 2^N states (in terms of switching operations).

Truth tables for switching functions. In logical control, the binary value of each possible output response or switching function $y_1, y_2, \ldots, y_N$, for each combination of binary input variables can be tabulated in what is known as a *truth table*. A truth table for one output response, y, to three binary variables, x_1, x_2 and x_3 is given in Table I-3.

Table I-3

x_1	x_2	x_3	y	x_1	x_2	x_3	y
0	0	0	0	1	0	0	0
0	1	0	0	1	1	0	1
0	0	1	1	1	0	1	1
0	1	1	0	1	1	1	1

In fact, the truth table shows the Boolean algebra relationship between variables and output responses, that is, a certain switching strategy, and may therefore serve as a decision algorithm.

The relationships tabulated in the above truth table are of the general form $y = f(x_1, x_2, x_3)$ which can readily be represented in terms of elementary Boolean functions. In turn, any Boolean function, however complex, may be stated as an expression, using the three elementary logical operations, namely the OR operation (logic addition), the AND operation (logic multiplication) and the NOT operation (logic negation). The symbolic representations for these operations and the respective truth tables are given below.

(1) OR operation (logic addition): $y = x_1 \vee x_2$ (Table I-4).
(2) AND operation (logic multiplication): $y = x_1 \cdot x_2$ (Table I-5).
(3) NOT operation (negation): $y = \bar{x}$ (Table I-6).

Table I-4

x_1	x_2	y
0	0	0
0	1	1
1	0	1
1	1	1

Table I-5

x_1	x_2	y
0	0	0
0	1	0
1	0	0
1	1	1

Table I-6

x	y
0	1
1	0

It may be shown that the Boolean algebra representation of Table I-3 is of the form

$$y = f(x_1, x_2, x_3) = (x_1 \cdot x_2) \vee (x_2 \cdot x_3)$$

This can be proved by compiling a truth table (Table I-7) directly from the equation

$$y = (x_1 \cdot x_2) \vee (\bar{x}_2 \cdot x_3)$$

Table I-7

x_1	x_2	x_3	$\bar{x}_2$	$x_1 \cdot x_2$	$\bar{x}_2 \cdot x_3$	$y = (x_1 \cdot x_2) \vee (x_2 \cdot x_3)$
0	0	0	1	0	0	0
0	1	0	0	0	0	0
0	0	1	1	0	1	1
1	0	0	1	0	0	0
0	1	1	1	0	1	0
1	1	0	0	1	0	1
1	0	1	1	0	1	1
1	1	1	0	1	0	1

and using the truth tables for the respective elementary functions. The result will be identical with that presented in Table I-3.

In the general case, the problem of finding an algorithm for switching operations reduces to finding functionals of the form

$$\left.\begin{aligned} y_1 &= f_1(x_1, x_2, x_3, \ldots, x_j, \ldots, x_N) \\ y_2 &= f_2(x_1, x_2, x_3, \ldots, x_j, \ldots, x_N) \\ y_3 &= f_3(x_1, x_2, x_3, \ldots, x_j, \ldots, x_N) \\ y_M &= f_M(x_1, x_2, x_3, \ldots, x_j, \ldots, x_N) \end{aligned}\right\} \qquad \text{(I-52)}$$

that will maintain the desired logical relationships between the combinations of input variables, x_1, x_2, ..., x_N, and the output responses, y_1, y_2, y_3, ..., y_M.

However, it is not always possible to use truth tables as a starting point for developing a decision algorithm in terms of Boolean algebra. In fact, such tables are applicable as long as the relationships between the variables are simple. With a great number of independent variables, this method becomes cumbersome as one has to tabulate all the possible combinations.

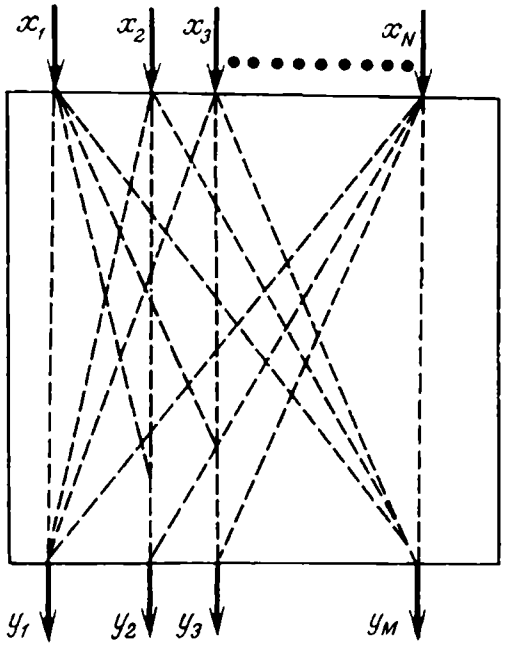


Fig. I-16. Input-output characterization of combinational logic

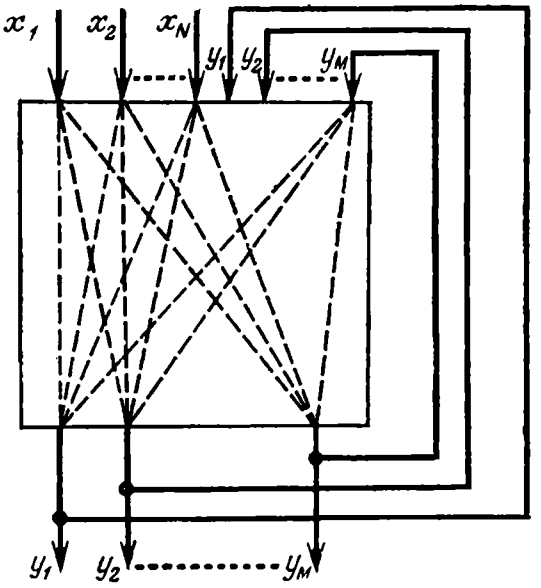


Fig. I-17. Feedback in a logical machine (sequential circuit)

For example, with $N = 10$, a truth table would have $2^{10} = 1024$ rows! Besides, truth tables can be compiled for only a limited class of logical machines with an unvariable internal state (combinational logic). In such machines, the output response or switching function, y, has a fixed value for each combination of input variables, x, (Fig. I-16), that is, the outputs are (ideally) functions of only the present condition of their inputs, regardless of their history.

Logical machines with memory. Most logical machines in use fall, however, in the category of discrete dynamic systems with memory. In behaviour, they exhibit outputs which depend on the past history of the inputs, and their internal state changes as the inputs change.

A further distinction of logical machines with memory is that their structure incorporates feedback (Fig. I-17). This fact is taken care of in the equations describing the decision algorithm of logical machines with memory:

$$\left.\begin{aligned} y_1 &= f_1(x_1, x_2, \ldots, x_N; y_1, y_2, \ldots, y_M) \\ y_2 &= f_2(x_1, x_2, \ldots, x_N; y_1, y_2, \ldots, y_M) \\ y_3 &= f_3(x_1, x_2, \ldots, x_N; y_1, y_2, \ldots, y_M) \\ y_M &= f_M(x_1, x_2, \ldots, x_N; y_1, y_2, \ldots, y_M) \end{aligned}\right\} \quad \text{(I-53)}$$

In Eqs. (I-53), the output-response symbols on the right-hand side $(y_1, y_2, \ldots, y_M)$ define the internal state of the system at the instant when a change occurs in any of the input variables, x_j.

Discrete memory element. The simplest logical machine realizing a feedback algorithm is a block containing a discrete memory element. It stores one bit of information and thus can at any time exist in one of two ("0" or "1") states.

A memory element may be described by an equation of the form

$$y = x_1 \vee (x_2 \cdot y)$$

Consider all the possible values of the output variable, y, that may be taken by a memory element according to the state of the input events, x_1 and x_2.

Case 1. Let the memory element initially be in a state such that $x_1 = 0$ and $x_2 = 0$. Then y must repeat the input information, that is, take on a value of 0, as follows from the equation

$$y = 0 \vee (0 \cdot y)$$

which turns to an identity of the form

$$0 = 0 \vee (0 \cdot 0)$$

Case 2. Now let $x_1 = 0$ and $x_2 = 1$. Then the equation of the memory element will take the form

$$y = 0 \vee (1 \cdot y)$$

Now y may take on a value of both 0 and 1. However, at the instant when $x_2 = 1$ is applied, $y = 0$, and so the identity takes the form

$$0 = 0 \vee (1 \cdot 0)$$

and y will retain the value of 0.

Case 3. Assuming that $x_2 = 1$ and $y = 0$, let $x_1 = 1$. Then

$$y = 1 \vee (1 \cdot y) = 1$$

The right-hand side of the equation should turn to 1 at any value of y. Thus, $y = 1$, and the equation reduces to an identity of the form

$$1 = 1 \vee (1 \cdot 1)$$

Case 4. Assuming that $y = 1$ and $x_2 = 1$, let $x_1 = 0$. Then the equation will be written as

$$y = 0 \vee (1 \cdot y)$$

Since $y = 1$, the identity should take the form

$$1 = 0 \vee (1 \cdot 1)$$

and y retains the value of 1. Thus the memory element stores $y = 1$ after x_1 becomes 0 again.

Case 5. In order to set y to 0, we assume $x_1 = 0$, let $x_2 = 0$. Then the equation will take the form

$$y = 0 \vee (0 \cdot y) = 0$$

and the identity will be restored to the form

$$0 = 0 \vee (0 \cdot 0)$$

From the foregoing it follows that the relationships between the input variables x_1 and x_2, on the one hand, and the output function y, on the other, are not fixed or univalued, as they are in systems without memory.

Because these relationships are many-valued (see Cases 2 and 4), one has to compile several truth tables for one feedback function of the form $y = f(x_1, x_2, y)$. However, such tables may only be used in a few very simple cases. As a rule, switching algorithms have to be stated directly in terms of symbolic logic from an analysis of the logical relationships between the variables involved and the decision strategy chosen.

Generally, analysis in terms of Boolean algebra is rather elaborate, and requires certain skills on the part of the designer. Yet, skills come with practice, while the method is the only one available in many cases for deriving a decision algorithm and presenting it in analytical form.

Minimization of Boolean functions. The last step in developing an algorithm for switching operations yields an analytical description in the form of logical expressions similar to (I-53). However, this representation may be too complicated for use in the synthesis of a workable system. Therefore, techniques are available to the logical-system designer which enable him to manipulate these complex functions so as to reduce them to a form calling for a minimum number of physical components.

Logical expressions are manipulated on the basis of the postulates and theorems of Boolean algebra. We shall take up some of them.

(1) The OR and AND operations have the properties of associativity:

$$\left.\begin{aligned} x_1 \cdot x_2 &= x_2 \cdot x_1 \\ x_1 \vee x_2 &= x_2 \vee x_1 \\ x_1(x_2 \cdot x_3) &= (x_1 \cdot x_2) \cdot x_3 \\ x_1 \vee (x_2 \vee x_3) &= (x_1 \vee x_2) \vee x_3 \end{aligned}\right\} \qquad \text{(I-54)}$$

Besides, they are distributive:

$$x_1(x_2 \vee x_3) = (x_1 \cdot x_2) \vee (x_1 \cdot x_3) \qquad \text{(I-55)}$$

$$x_1 \vee (x_2 \cdot x_3) = (x_1 \vee x_2) \cdot (x_1 \vee x_3) \qquad \text{(I-56)}$$

Equations (I-54) and (I-55) resemble analogous equations in conventional algebra. Eq. (I-56) has no equivalence in conventional algebra.

(2) Boolean operations also obey the following simple, but very important relations:

$$\left.\begin{array}{ll} \overline{(\bar{x})} = x & x \cdot \bar{x} = 0 \\ x \vee x = x & x \vee 1 = 1 \\ x \cdot x = x & x \vee 0 = x \\ x \vee \bar{x} = 1 & x \cdot 0 = 0 \end{array}\right\} \tag{I-57}$$

(3) Very often, complicated Boolean functions can be simplified by means of the following relations:

$$\left.\begin{array}{l} x_1 \cdot x_2 = \overline{\bar{x}_1 \vee \bar{x}_2} \\ x_1 \vee x_2 = \overline{\bar{x}_1 \cdot \bar{x}_2} \end{array}\right\} \tag{I-58}$$

The respective truth tables for each of Eqs. (I-58) are I-8, I-9, and I-10, I-11.

Table I-8

x_1	x_2	$x_1 \cdot x_2$
0	0	0
0	1	0
1	0	0
1	1	1

Table I-9

x_1	x_2	$\bar{x}_1$	$\bar{x}_2$	$x_1 \vee \bar{x}_2$	$\overline{\bar{x}_1 \vee \bar{x}_2}$
0	0	1	1	1	0
0	1	1	0	1	0
1	0	0	1	1	0
1	1	0	0	0	1

Table I-10

x_1	x_2	$x_1 \vee x_2$
0	0	0
0	1	1
1	0	1
1	1	1

Table I-11

x_1	x_2	$\bar{x}_1$	$\bar{x}_2$	$\bar{x}_1 \cdot \bar{x}_2$	$\overline{\bar{x}_1 \vee \bar{x}_2}$
0	0	1	1	1	0
0	1	1	0	0	1
1	0	0	1	0	1
1	1	0	0	0	1

Equations (I-58) have two corollaries:

$$\left.\begin{aligned} \bar{x}_1 \cdot \bar{x}_2 &= \overline{x_1 \vee x_2} \\ \bar{x}_1 \vee \bar{x}_2 &= \overline{x_1 \cdot x_2} \end{aligned}\right\} \qquad \text{(I-59)}$$

Now that we have learned a few basic facts about Boolean algebra, we shall be in a position to consider a specific problem.

Developing a decision algorithm. As already noted, a very convenient example for our purpose is offered by a contact reactor of the type used in catalytic processes.

Example I-4. We seek an optimum switching strategy for a contact-reactor department which, from a switching point of view, has K parallel lines of m reactors in each, so that the total number of reactors is Km. All reactors operate on a batch basis (with each cycle consisting of a contact phase followed by regeneration and again by a contact phase), so that only some reactors are in the contact phase at any instant. The basic quantitative indices of reactor performance are: contact time, regeneration time, reactor throughput, fractional conversion, regeneration cost, and profit per unit of product.

The goal of an optimum switching strategy is to maximize (or minimize) a decision criterion determined inferentially from the reactor performance indices.

Such a criterion may advantageously be the average profit R per unit of product over a time interval τ:

$$R(\tau) = \frac{\int_0^{\tau} [Fxc_1 - Qc_2 - Fc_3 - c_4]\, d\tau - P}{\tau + \Delta\tau_{reg}} \qquad \text{(I-60)}$$

where F is the amount of raw material expended, x is the fractional conversion, c_1 and c_2 are the costs of the respective products, c_3 is the specific cost of materials handling, c_4 is the fixed overhead, P is the cost of regeneration, Q is the amount of heat required to sustain the reaction, $\Delta\tau_{reg}$ is the shut-down time for catalyst regeneration.

The above integral expression is an extremal function in which the average profit R attains its extremal value at the end of a certain time interval τ_{opt}. This time interval, τ_{opt}, measured from the instant when a reactor is started up to the instant when the reactor reaches its maximum performance, may be regarded as an optimum contact time under the specified operating conditions (Fig. I-18).

Because of the ageing of the catalyst, stochastic changes in the quality of the source materials, and variations in thermal load, the peak of the average profit function continually drifts relative to the time axis (Fig. I-19). Accord-

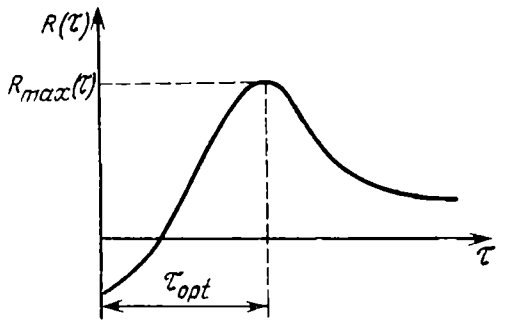


Fig. I-18. Average profit as a function of time

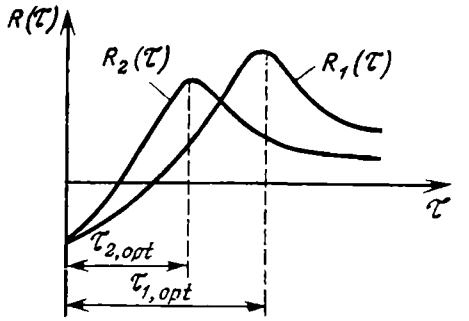


Fig. I-19. Drift in the extremum value of the average profit

ingly, the optimum contact time is different for each reactor and for each contact cycle.

This is why an optimum switching strategy must be formulated on the assumption that there is an optimum contact interval for each ith reactor (in terms of a maximum profit per operation).

Assuming an optimum utilization of the reactors, the switching strategy may be formulated as follows:

(1) Reactors should be switched so that at any instant there is a constant number of reactors in the contact phase.

(2) As a reactor is switched out of the regeneration phase, another one reaching the end of an optimum contact time, $\tau_{opt,\,i}$, earliest of all, should be put into the regeneration phase.

The last requirement may serve as a switching criterion.

For a better insight into the problem, a few simplifications are in order. Assume that a given control system can provide an optimum switching strategy for the reactors in one line only. Then, only one reactor will be in the regeneration phase at any given instant, the remaining $m-1$ reactors being in the contact phase.

With this assumption there must be an independent optimum control system for each line. It is obvious that there will be as many identical control systems as there are reactor lines.

Reactors are switched out of operation for catalyst regeneration by a signal coming from a device which determines the daily average profit $R(\tau)$, using Eq. (I-60). When the function $R(\tau)$ attains its peak, the device generates

a signal indicating that the respective reactor is ready to be switched to regeneration. If the previous reactor has not yet completed regeneration, the "ready" one queues up and keeps operating for some time.

Because of the difference in the optimum switching time, τ_{opt}, between the various reactors, several reactors may generate a "ready-to-regenerate" signal while a previous one has not yet completed regeneration. In such a case, the "ready" reactors should queue up in the order of their signals. This implies that the control system has to perform one more function—that of storing the "ready" signals in the correct sequence.

At the end of a regeneration cycle, the reactor that has been regenerated takes over and carries the load, and its place is taken by the reactor which is at the head of the queue. By this instant the awaiting reactor will have moved farther away from its optimum condition than the reactors down the queue, and it would be disadvantageous to put it back on stream in the same sequence.

Now that we have defined the switching criterion and the switching strategy in verbal form, we may proceed with developing the decision algorithm in terms of Boolean algebra. To simplify the matter, we shall examine a simple case involving two reactors per line, with one reactor being in the contact phase and the other in the regeneration phase.

Let x_1 be the signal from the device computing the function $R(\tau)$ for the first reactor, and x_2 be the signal from a similar device computing the same function for the second reactor. The signals x_1 and x_2 take a value of "0" if the functions $R_1(\tau)$ and $R_2(\tau)$ have not yet reached their peak values, and a value of "1" when the functions pass through their peaks. These "1" values of the signals x_1 and x_2 are stored until the respective reactor completes its regeneration phase.

Let y_1 and y_2 be the signals which cause the reactors to switch to regeneration. The signal y_1 takes on a value of "1" when the first reactor may switch to regeneration. Similarly, the second reactor may switch to regeneration when $y_2 = 1$.

From the statement of the problem it follows that the variable y_1 may take a value of "1" only at $x_1 = 1$ (that is, in the presence of a "ready" signal for the first reactor). Accordingly, $y_2 = 1$ may only happen at $x_2 = 1$.

A further requirement that must be satisfied is as follows. If the first reactor is switched to regeneration first and $y_1 = 1$, then an "inhibit" condition should be imposed on the second reactor. That is, the condition $y_2 = 0$ must be maintained until the first reactor completes regeneration. In terms of Boolean algebra, this may be expressed as

$$y_2 = x_2 \cdot \bar{y}_1 \tag{I-61}$$

The same reasoning applies to a case where the second reactor is switched to regeneration first:

$$y_1 = x_1 \cdot \bar{y}_2 \tag{I-62}$$

From the above two equations one can readily derive a decision algorithm for two reactors. This algorithm realizes a decision strategy according to the

"first come—first served" principle. Let us test this algorithm under various combinations of arguments:

(1) Let the signal that comes first be $x_1 = 1$. Since at the previous instant $x_2 = 0$, then $y_2 = 0 \cdot y_1 = 0$. Thus, $\bar{y}_2 = 1$. Therefore, in Eq. (I-62) we get

$$y_1 = 1 \cdot 1 = 1$$

With this combination of signals, the first reactor will be switched to regeneration first.

(2) Now let the signal $x_2 = 1$ follow the signal $x_1 = 1$. This is a situation in which the second reactor is ready to switch to regeneration, but the first one has not yet completed it. Then $y_1 = 1$, and $\bar{y}_1 = 0$, and $\bar{y}_2 = 1 \cdot 0 = 0$. In other words, the second reactor will not be allowed to switch to regeneration until the first completes it.

3. When the first reactor completes regeneration, the signal x_1 will again take a value of "0". Then $y_1 = 0 \cdot \bar{y}_2 = 0$, whence $y_1 = 1$. Since the signal $x_2 = 1$ is retained, then $y_2 = 1 \cdot 1 = 1$, and the second reactor is switched to regeneration.

4. If, now, the signal $x_1 = 1$ comes while the second reactor has not completed regeneration yet, the first reactor will queue up. In other words, $\bar{y}_2 = 1$ and $\bar{y}_2 = 0$. Hence, $y_1 = 1 \cdot 0 = 0$ at $x_1 = 1$. That is, the first reactor queues up.

Now consider the general case involving a line of m reactors one of which is under regeneration at each instant of time. Of the m reactors, any one, say the jth reactor, can generate a "ready" signal. Under the conditions of the problem, the signal y_j should inhibit switching of all the remaining $m-1$ reactors to regeneration. To satisfy the requirement, the signal y_j must impose the "first come—first served" decision constraint on the y-signals of all the remaining $m-1$ reactors. This constraint can be described by appropriate equations as follows:

— for the jth and 1st reactors:

$$\left.\begin{aligned} y_j^1 &= x_j \cdot \bar{y}_1^j \\ y_1^j &= x_1 \cdot \bar{y}_j^1 \end{aligned}\right\} \qquad \text{(I-63)}$$

— for the jth and 2nd reactors:

$$\left.\begin{aligned} y_j^2 &= x_j \cdot \bar{y}_2^j \\ y_2^j &= x_2 \cdot \bar{y}_j^2 \end{aligned}\right\} \qquad \text{(I-64)}$$

— for the jth and mth reactors:

$$\left.\begin{aligned} y_j^m &= x_j \cdot \bar{y}_m^j \\ y_m^j &= x_m \cdot \bar{y}_j^m \end{aligned}\right\}$$

In the above equations, the superscript of the variable y designates the reactor to which the "first come—first served" principle applies. The subscript designates, as before, the reactor to which a given control signal is fed.

From the consideration of the equations for the jth reactor it follows that:

(1) The variable y_j^j may take a value of "1" if the jth reactor generates a "ready" signal before the first reactor. In other words, at the instant of arrival of the signal $x_j = 1$, we shall have $x_1 = 0$. Then

$$y_1^j = x_1 \cdot \bar{y}_j^1 = 0 \cdot \bar{y}_j^1 = 0$$

and

$$\bar{y}_j^1 = x_j \cdot \bar{y}_1^j = 1 \cdot 1 = 1$$

(2) The variable y_j^2 may take a value of "1" if the jth reactor generates a "ready" signal before the second reactor. By analogy with the previous situation, it may be said that $y_j^2 = 1$, $y_2^j = 0$, etc.

Generally, the variable y_j^m may take a value of "1" if the jth reactor generates a "ready" signal before the mth reactor. Then, $y_j^m = 1$ and $y_m^j = 0$.

From the statement of the problem, in order that the jth reactor can be put under regeneration, its "ready" signal must come ahead of the "ready" signals from all the other reactors. In other words, y_j^i must take a value of "1" always, where $i = 1, 2, 3, \ldots, j-1, j+1, \ldots, m$. If, on the other hand, at least one "ready" signal from, say, the lth reactor comes first, the jth reactor must queue up rather than switch to regeneration. For this situation, $y_j^l = 0$ and $y_l^j = 1$.

Let z_j designate the output control signal for the jth reactor. According to the switching strategy set forth above, the variable z_j is connected to the variables y_j^i (where $i = 1, 2, 3, \ldots, j-1, j+1, \ldots, m$) by the following equation:

$$z_j = y_j^1 \cdot y_j^2 \cdot y_j^3, \ldots, y_j^{j-1} \cdot y_j^{j+1}, \ldots, y_j^m$$

Indeed, $z_j = 1$, only if all terms y_j^i (where $i = 1, 2, 3, \ldots, j-1, j+1, \ldots, m$) take a value of "1". If, on the other hand, at least one of the terms, y_m^j, takes a value of "0", z_j will turn to 0, too.

Since the index j may take any value ($j = 1, 2, 3, \ldots, m-1, m$), the following system of equations may be written for all z_j reactors:

$$\left.\begin{aligned}
z_1 &= y_1^2 \cdot y_1^3 \ldots y_1^j \ldots y_1^m \\
z_2 &= y_2^1 \cdot y_2^3 \ldots y_2^j \ldots y_2^m \\
&\ldots\ldots\ldots\ldots\ldots\ldots \\
z_j &= y_j^1 \cdot y_j^2 \ldots y_j^{j-1} \cdot y_j^{j+1} \cdot y_j^m \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
z_{m-1} &= y_{m-1}^1 \cdot y_{m-1}^2 \ldots y_{m-1}^j \ldots y_{m-1}^{m-2} \cdot y_{m-1}^m \\
z_m &= y_m^1 \cdot y_m^2 \ldots y_m^j \ldots y_m^{m-1}
\end{aligned}\right\} \qquad \text{(I-65)}$$

In this system of equations, all y-variables are interrelated by a set of equations of the form:

$$\left.\begin{aligned}
y_j^i &= x_j \cdot \bar{y}_i^j \\
y_i^j &= x_i \cdot \bar{y}_j^i
\end{aligned}\right\} \qquad \begin{aligned} j &= 1, 2, 3, \ldots, m \\ i &= 1, 2, 3, \ldots, m \end{aligned}$$

These are *constraint equations.*

The total number of constraint equations for m reactors may be found as follows. Every two reactors are interrelated by two constraint equations. Since the number of pairs that can be made out of the number m is equal to the number of possible combinations of m elements taken two at a time, that is, to $A_m^2 = [m(m-1)]/2$, the total number of constraint equations will be

$$2A_m^2 = m(m-1) \tag{I-66}$$

In logic-diagram form, the decision algorithm obtained analytically for $m = 3$ can be drawn up as shown in Fig. I-20.

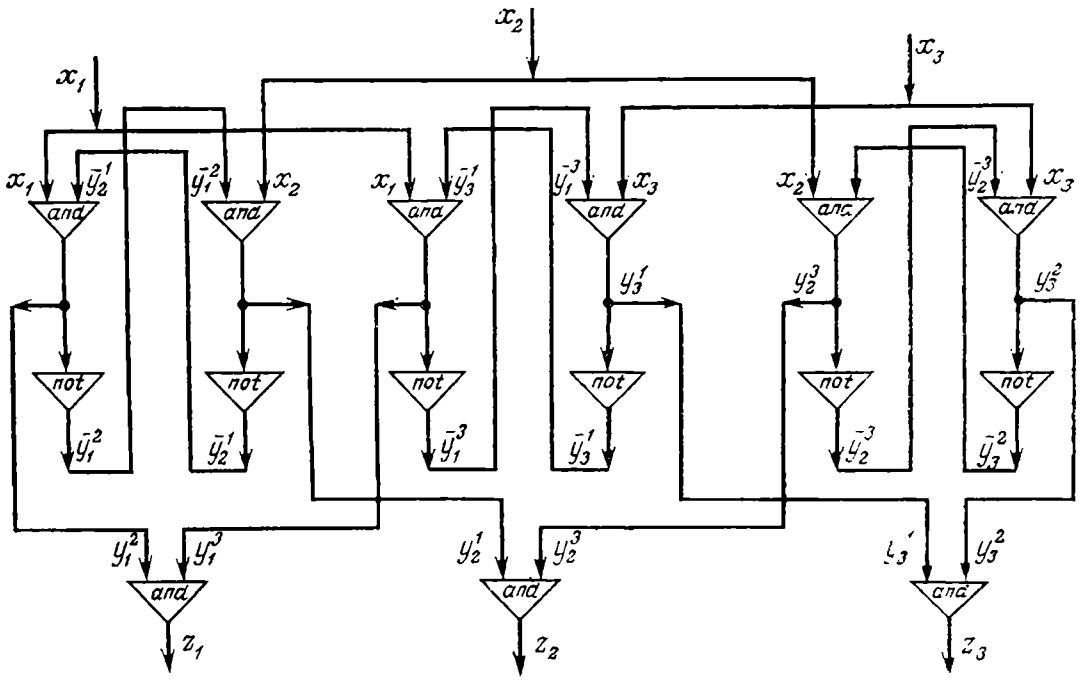


Fig. I-20. Logic diagram for control of three reactors

Realization of control logic. The decision algorithm derived in Example I-4 may be realized by a network obtained by interconnecting physical units which mechanize the AND and NOT functions (AND and NOT gates) in accordance with the logic diagram of Fig. I-20.

In a way, synthesis of a logical control machine on the basis of a logic diagram is not unlike developing a problem set-up for the simulation of a continuous process on an analog computer.

The physical units that are to go into the resulting logical control network or logical machine, should be specified in advance. Among other things, they should satisfy the requirement of *functional completeness*, so that any algorithm, however complicated, may be fully executed.

We say that a set of gates is *functionally complete* if any Boolean function can be realized using gates from that set. Thus the set AND, OR, NOT

is functionally complete, as any logical (decision) algorithm can be resolved into these three logical functions. In fact, some physical units used in the synthesis of logical control networks or machines have still greater functional capabilities and can even realize combinations of elementary Boolean functions. Such elements permit flexibility and economy in mechanizing a control system and enhance its reliability. When a functionally complete set has only one gate, we say that the gate is *universal.*

One such universal element is the *pneumatic relay*. Among its advantages are high reliability, stability, simple maintenance, and freedom from explosion and fire hazards. In short, it meets all the requirements that a control-system element used in chemical manufacture should satisfy. This is why pneumatic relays will figure as a basic logical element in all subsequent examinations concerned with the synthesis of logical networks mechanizing a particular decision algorithm.

The two-nozzle pneumatic relay shown in sketch form in Fig. I-21 has three diaphragms made fast to a stem. The diaphragms form four chambers, *a*, *b*, *c* and *d*. Chambers *b* and *c* are inlet chambers which accept signals x_3 and x_4. Chambers *a* and *d* are interconnected from the outside when the relay is placed in circuit, and they deliver an output signal, *y*.

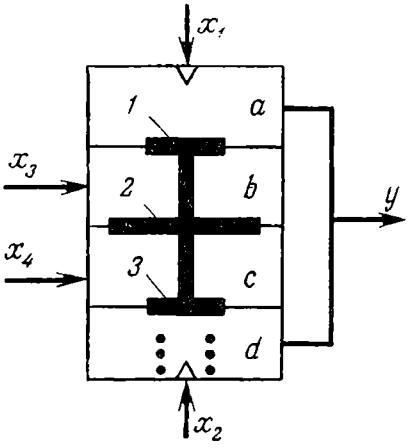


Fig. I-21. Two-nozzle pneumatic relay

The effective areas of top diaphragm *1* and of bottom diaphragm *3* are half as large as that of middle diaphragm *2*. When a positive-pressure signal of 1 atm is admitted into one of the inlet chambers, say chamber *b*, a force is exerted on each of diaphragms *1* and *2* so that they tend to flex in opposite directions. The force F_1 directed upwards is $F_1 = 1\ \text{atm} \times S_1$, where S_1 is the effective area of the top diaphragm. The force directed downwards is $F_2 = 1\ \text{atm} \times S_2$, where S_2 is the effective area of the middle diaphragm. Since $S_2 = 2S_1$, the resultant force acts downwards and is equal to $R_b = F_2 - F_1 = 1\ \text{atm} \times (S_2 - S_1) = 1\ \text{atm} \times S_1$.

In the absence of 1-atm control signals in chambers *b* and *c*, the diaphragm unit is set by a spring to the initial position in which the top nozzle is closed and the bottom nozzle is open.

When a signal, $x_3 = 1$ atm, is admitted into chamber *b*, the force R_b overcomes the force of the spring and moves the diaphragm unit downwards, thereby opening the top nozzle and closing the bottom nozzle. If, now, a signal $x_4 = 1$ atm be admitted to chamber *c*, the resultant force R_c will be directed upwards. Since R_b is equal to R_c, but acts in the opposite direction, they cancel out, and the spring sets the diaphragm unit to the upper position again.

The relay shown in Fig. I-21 mechanizes a Boolean function of four variables, $y = f(x_1, x_2, x_3, x_4)$. This function may be evaluated by analysing operation of the relay.

The position of the diaphragm unit is decided by the relative magnitudes of signals x_3 and x_4. We introduce a function, $z = f(x_3, x_4)$, to describe all the possible states of the diaphragm unit. Let $z = 0$ when the spring causes the diaphragm unit to take up the upper position. Then $z = 1$ will correspond to the down position of the diaphragm unit.

The value of the output signal y as a function of the position of the diaphragm unit may be described by a Boolean expression of the form

$$y = x_1 \cdot z \vee x_2 \cdot \bar{z}$$

Indeed, when $z = 0$ (the diaphragm unit takes up the upper position), the signal appearing at the relay outlet is x_2. This situation is described by the expression

$$y = x \cdot 0 \vee x_2 \cdot 1 = x_2$$

At $z = 1$ (the diaphragm unit is in the down position), the top nozzle is open, and the signal x_1 appears at the relay outlet. This situation is described by the expression

$$y = x_1 \cdot 1 \vee x_2 \cdot 0 = x_1$$

Now we shall analyse the function $z = f(x_3, x_4)$. The diaphragm unit may take up the down position ($z = 1$) only if $x_3 = 1$ and $x_4 = 0$. This interrelation of the signals may be described as

$$z = x_3 \cdot \bar{x}_4$$

Substituting the expression for z in the original equation for y, we obtain

$$y = x_1 \cdot z \vee x_2 \bar{z} = [x_1(x_3 \cdot \bar{x}_4)] \vee [x_2(x_3 \cdot x_4)]$$

Using Eq. (I-58) for simplification, we finally get

$$y = [x_1 \cdot x_3 \cdot \bar{x}_4] \vee [x_1(\bar{x}_3 \vee x_4)] \tag{I-67}$$

In special cases, the Boolean functions can be simplified by assigning constant values to some variables. Let the bottom nozzle communicate with the atmosphere. Then $x_2 = 0 =$ constant, and $y = x_1 \cdot x_3 \cdot \bar{x}_4$. If, on the other hand, we set $x_1 = 0 =$ constant (that is, the top nozzle is vented to the atmosphere), then $y = x_2(\bar{x}_3 \vee x_4)$. Further simplifications can be secured by putting x_1 and x_2 in turn identically equal to 1 (the nozzle is permanently connected to the pressure supply line).

Now we shall examine control logic mechanization, using the pneumatic relay as the basic logical element. For simplicity, we shall limit our discussion

to a decision algorithm for three reactors; it should be remembered, however, that the same technique is applicable to any number m of reactors, however great.

According to the foregoing, the decision algorithm for $m = 3$ in Boolean algebraic representation is as follows

$$\left.\begin{aligned} z_1 &= y_1^2 \cdot y_1^3 \\ z_2 &= y_2^1 \cdot y_2^3 \\ z_3 &= y_3^1 \cdot y_3^2 \end{aligned}\right\} \tag{I-68}$$

In the above relations, the functions y are derived from the constraint equations which have the following form

$$\left.\begin{aligned} y_1^2 &= x_1 \cdot \bar{y}_2^1 \\ y_2^1 &= x_2 \cdot \bar{y}_1^2 \end{aligned}\right\} \tag{I-69}$$

$$\left.\begin{aligned} y_1^3 &= x_1 \cdot \bar{y}_3^1 \\ y_3^1 &= x_3 \cdot \bar{y}_1^3 \end{aligned}\right\} \tag{I-70}$$

$$\left.\begin{aligned} y_2^3 &= x_2 \cdot \bar{y}_3^2 \\ y_3^2 &= x_3 \cdot \bar{y}_2^3 \end{aligned}\right\} \tag{I-71}$$

These constraint equations need simplification so that they can be mechanized with pneumatic relays. On substituting the expression for y_1^3 from the constraint equation in that for z_1, we obtain

$$z_1 = x_1 \cdot y_1^2 \cdot \bar{y}_3^1$$

Similarly, on substituting the expression for y_2^1 in that for z_2 and for y_3^2 in that for z_3, we get

$$z_2 = x_2 \cdot \bar{y}_1^2 \cdot y_2^3$$

and

$$z_3 = x_3 \cdot y_3^1 \cdot y_2^3$$

Finally, we obtain a system of three simultaneous equations

$$\left.\begin{aligned} z_1 &= x_1 \cdot y_1^2 \cdot \bar{y}_3^1 \\ z_2 &= x_2 \cdot \bar{y}_1^2 \cdot y_2^3 \\ z_3 &= x_3 \cdot \bar{y}_3^1 \cdot \bar{y}_2^3 \end{aligned}\right\} \tag{I-72}$$

These equations are in six variables, x_1, x_2, x_3, y_1^2, y_3^1 and y_2^3, of which x_1, x_2 and x_3 are independent variables, while y_1^2, y_3^1 and y_2^3 are themselves functions which should be evaluated. This can be done through the use of constraint equations. On substituting $y_2^1 = x_2 \cdot y_1^2$ in $y_1^2 = x_1 \cdot y_2^1$ in the first pair of equations we obtain

$$y_1^3 = x_1 \cdot \bar{y}_2^1 = x_1 \overline{(x_2 \cdot \bar{y}_1^2)} = x_1 (\bar{x}_2 \vee y_1^2)$$

Similar substitutions in the second and third pairs give

$$y_3^1 = x_3(\bar{x}_1 \vee y_3^1)$$

and

$$y_2^3 = x_2(\bar{x}_3 \vee y_2^3)$$

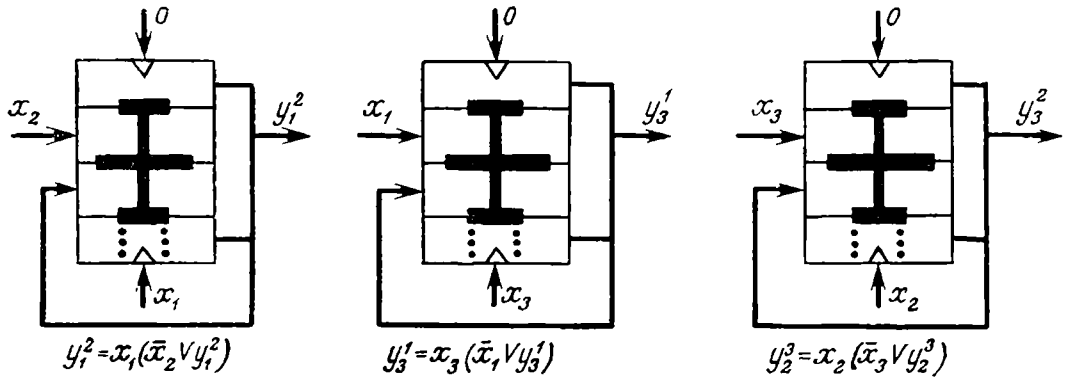


Fig. I-22. Connections of a pneumatic relay in a feedback circuit

From the final expressions it may be concluded that the control system in question is one with memory, because the right-hand sides of the equations contain y-functions.

The equations for y_1^2, y_3^1 and y_2^3 describe a pneumatic relay connected in a feedback circuit (Fig. I-22). The relay circuits mechanizing the equations for z_1, z_2 and z_3 are shown in Fig. I-23.

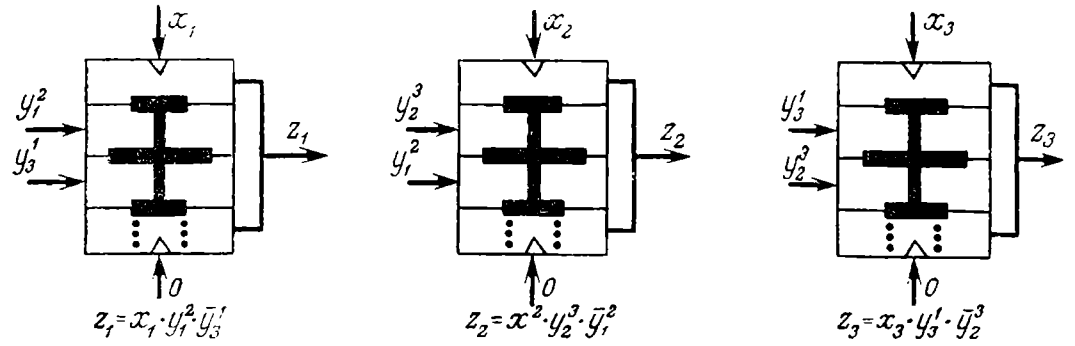


Fig. I-23. Connections of a relay to realize decision algorithms z_1, z_2 and z_3

In view of interactions between the signals, we finally obtain the circuit shown in Fig. I-24. This circuit realizes the decision algorithm for three reactors. At $m > 3$, the circuit should be elaborated in accordance with the developed algorithm and the circuit configurations for individual relays.

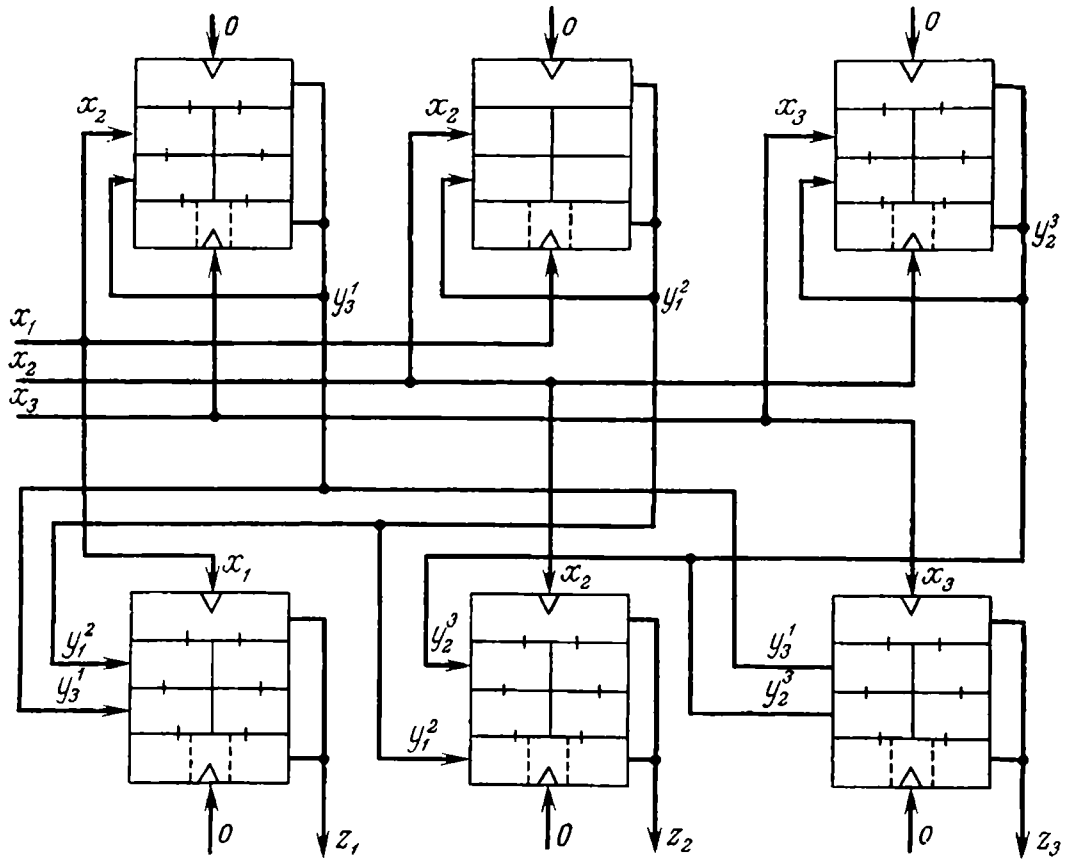


Fig. I-24. Realization of a decision algorithm for three reactors

(B) BASIC FORMS OF COMPUTER CONTROL FOR CHEMICAL ENGINEERING SYSTEMS

As already noted, an example of a large-scale cybernetic system is a chemical factory. With such systems, it is best to use computer control.[18-26]

As has been stressed more than once, a distinction of any chemical process is that it usually involves several significant controlled variables. Therefore, simple single-loop control systems cannot maintain the process sufficiently close to its optimum. In other words, the need arises for multivariable, multiloop systems, which is another way of stating the need for integrated automation. Here, the term *integrated automation* designates a complex of automatic systems which carry on advanced forms of industrial control where the human operator only keeps watch on the performance of these systems and the state of the controlled plant.

In this context, the problems of integrated automation and control call for a fundamentally new approach. At present, this is the use of cybernetic methods, namely mathematical formalization of processes and computers. With existing high-speed computers, it is practicable to build multiloop systems capable of continuously monitoring a process and deriving all the necessary process variables (mass flow rate, per cent contents, etc.) from

updated information in order to optimize the process through a comparison with its mathematical model, and not only to maintain it in predetermined dynamic relationships.

In some cases, computer control may lead to a drastic overhaul of the entire process and its management through the adoption of faster and more sophisticated production schemes, novel physical and chemical methods based on high-speed interactions which cannot be kept under control by conventional means.

When ganged up with other automatic control facilities, special- and general-purpose digital and analog computers will greatly help with integrated automation of the most intricate manufactures and serve as a basis for fully automated departments and plants. The success or failure of such projects will depend on how efficient the man-computer-plant system can be made.

At present, the following forms of computer control are becoming prominent at the second and third levels of the control hierarchy: (1) direct digital control; (2) multiloop computer control; (3) optimizing computer control; (4) self-adjusting computer control; and (5) adaptive computer and learning control.

Direct digital control. The idea of on-line digital computer control came with fast advances in computer engineering, notably with the increased availability of digital computers. The desire to reduce the cost of digital computers used to optimize industrial processes prompted their wider employment instead of conventional monitoring and control facilities. A further backing for the idea came from the fact that digital measuring techniques had already been adopted for most process variables.

The crucial problems in the development of direct digital computer control have been those of data quantization and sampling, that is, the conversion of continuous signals into discrete ones on the basis of Kotelnikov's theorem (see p. 28); the choice of optimum sampling time and optimum rate of calculations done by digital controllers according to process dynamics and the controller action used; development of operating procedures and control algorithms.

A simplified block-diagram of a DDC system appears in Fig. I-25. The inputs to the system originate in the process variables. Measuring elements (transducers), T, convert the signals into suitable electric or pneumatic form. Via an input sampling switch, S, the inputs are then routed to an analog-to-digital converter, A/D, whence the signals are applied in digital form to a digital computer, DC, to be "written" into its memory. The digital computer, which acts as a multi-loop controller, operates on the inputs to a predetermined program and produces control signals which are converted to analog form by a digital-to-analog converter, D/A, and distributed by an output sampler, S, among the respective hold circuits, HC, which store the control signal for the duration of the control interval, T, that is, until arrival of the next value of the control signal. From each hold circuit the control signal is routed to the associated final control element, FC.

Thus, each control loop is closed only for a time T/n, where n is the number of control loops. The computer may be programmed for either independent or interconnected operation of the control loops.

As a way of enhancing reliability, simplifying the computation by the digital computer, and securing a gradual transition from manual to automatic control, DDC systems utilize signals representing changes in, rather than the absolute final control position of the element.

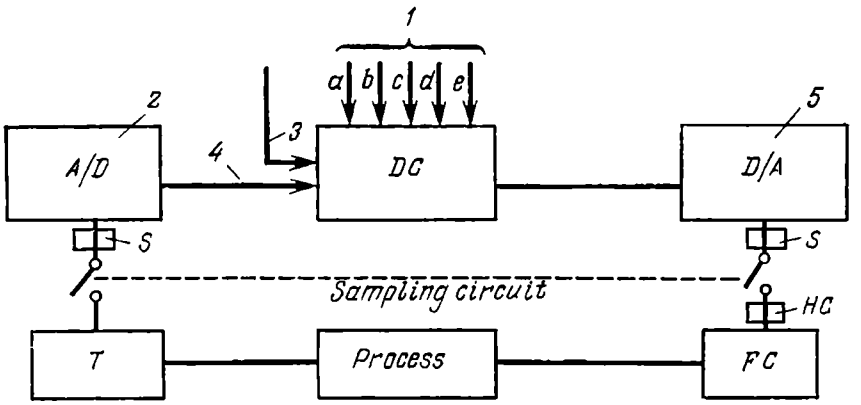


Fig. I-25. Digital computer control system

1 — controller settings: (*a*) proportional; (*b*) integral; (*c*) differential; (*d*) and (*e*) other forms; *2* — *A/D* converter; *3* — set-point; *4* — sampled variable; *5* — *D/A* converter; *A* — analog signal; *D* — digital (discrete) signal; *T* — transducer; *FC* — final control; *S* — sampling switch; *HC* — hold circuit

The settings of digital controllers are computed at regular intervals and without difficulty, because the computations are done by the computer to a program.

The sampling time in a DDC system should preferably be made as long as practicable. Apart from a better utilization of physical facilities, this makes less stringent the requirements for the associated digital computer, the speed of operation (multiplication), and computations. Furthermore, with a long sampling interval, the same system may serve a greater number of loops and have a simpler configuration without any sacrifice in the quality of control.

On the other hand, a control loop must respond to any changes in the set-point without delay. Theoretically, the response to a control action might be initiated the same instant as a change is made in the set-point, if this does not render operation of the system asynchronous and considerably complicate computer programming. In an emergency, too, corrective action, automatic or manual, should preferably be started at once. As a result, the time interval between a measurement and computation reduces to a minimum. Under the circumstances, if the noise frequency happens to be close to the sampling rate or its harmonics, noise in the measuring (or monitoring) system might lead to a false readout from the computer and to a deviation of the measured variable from its true value. Hence, the input signal must of necessity be smoothed or filtered in order to reduce measurement noise.

The minimum sampling time for a DDC system for fluid flows is 1.5 s, and the maximum one (applying to emergencies) should not exceed 10 to 20 s. Generally, the sampling interval should be chosen on the basis of the ratio T/τ, where T is the process time constant and τ is the sampling time. At $T/\tau < 3$, a DDC system will show an unstable behaviour under transient conditions, while at $T/\tau = 3.2$ to 10, the process will be stable and unvarying in quality. Investigations have shown that the accuracy of direct digital control is sufficient, if the sample size is 1/1000.

The central control console of a DDC system usually has the following functions and input/output instrumentation:

1. Indication of process variables, controller settings, off-normal limits, and alarm settings.
2. Digital input devices operating on time-sharing basis for controller and alarm settings.
3. Recording of measured variables and off-normal indications.
4. Control-loop off-normal condition indication.
5. Final-control position indication.
6. Final-control selection (manual or automatic).
7. Final-control remote control panels.
8. Analog indication and recording.
9. Equipment shut-down indication and alarms.

Direct digital computer control systems are centralized systems. Owing to this, less floor area is taken up by instrument boards in the production departments, while the concentration of all inputs and outputs on a single central control panel contributes to a more efficient process control.

Direct digital control markedly improves the quality of control because the settings are precise and show no tendency to drift. Control is amazingly flexible because all control functions are performed by computer programs which can readily be changed or modified. Any change in the control algorithm involves no additional components. For example, proportional control can readily be replaced with integral control even in the case of non-linear processes.

Algorithms for direct digital control are compatible with those of optimizing, adaptive or programmed computer control. In fact, a digital control computer may be programmed to execute operating procedures too expensive for, or non-executable by, an analog computer. In terms of reliability, too, direct digital computer control is superior to analog computer control. This also applies to the testing and reduction of experimental data.

Multiloop control systems. For the most part, chemical-engineering processes are interacting processes. Their control involves the use of multiloop control systems. The simplest among them are *cascade control systems.* A cascade control system may be defined as one in which the output of one controller adjusts the set-point of another. Most often, a cascade control system consists of two or three stages.

In this connection, a good deal of interest, both academic and technological, is evoked by methods for reducing multiloop control systems to simpler

ones. After appropriate simplifications at the block-diagram level the problem arises to approximate high-order mathematical models with lower-order equations. A very important point is the determination of the dynamic behaviour, because a disturbance applied for test purposes to one loop inevitably brings about transients in the inputs and outputs of other loops.

Optimizing control systems. In the synthesis of an optimizing control system, one is concerned with steady-state (static) or unsteady-state (dynamic) optimization.

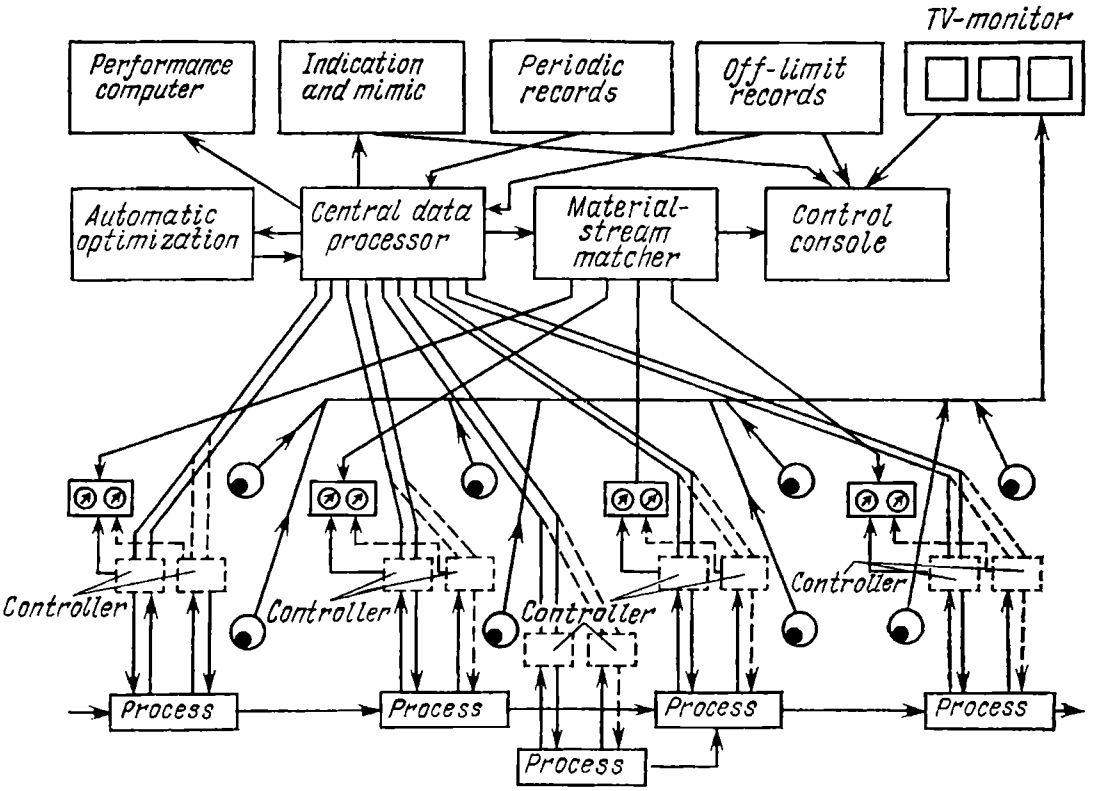


Fig. I-26. Computer control at the static process optimization level

With *steady-state optimization*, as its name implies, the process is assumed to be under steady-state conditions and may instantaneously be moved to a new steady state, if changes in load conditions demand so, with the aid of a conventional or an optimizing computer.

Where knowledge of a process is sufficiently complete and the problem is purely mathematical, one solves the problem through the use of a mathematical model of the process and a conventional computer. If a steady-state model of the process cannot be constructed, use is made of a "pure search" (direct-approach) method realized by an optimizing computer, or an automatic optimalizer. As a further alternative, a combination of both (Fig. I-26) may be used.

With the "pure search" (direct-approach) method, the system inputs are manipulated according to the observed effects of previous input changes on

the system performance until an optimum performance is secured. A major drawback of this method is a decrease in efficiency as the number of variables is increased (because the search takes a longer time). Also, since the objective is to minimize or maximize several variables, the optimizing computer must of necessity be rather elaborate in organization. Last but not least, the method is subject to noise, and the quality of the search depends on the dynamic behaviour of the process.

With a combination of the two methods, the mathematical description may be scanty and less accurate; yet the efficiency of the search is improved materially: a mathematical model defines the location of the optimum in rough terms, and direct testing on the controlled system finalizes the optimum.

As already noted, in steady-state optimization, the process is assumed to be in a steady state. Suppose that the performance criterion is the production cost. The cost function may be written as

$$q = q(y_1, \ldots, y_v, \ldots, y_n; u_1, \ldots, u, \ldots, u_m; p_1, \ldots, p_q) \qquad \text{(I-73)}$$

or as

$$q = q(u_1, \ldots, u, \ldots, u_m; z_1, \ldots, z_n, \ldots, z_p; p_1, \ldots, p_q) \qquad \text{(I-74)}$$

where $p_1, \ldots, p_q$ are the prices of the reaction products and source materials, y is the output variable, u is the manipulated variable and z is the disturbance.

With z_n and $p_1, \ldots, p_q$ held constant, the cost function depends on the independently manipulated variables. In such a case, it may be depicted as a surface in an $(m+1)$-dimensional space. For finite values of u, the quantity q may have no or several minima.

Steady-state optimization is applicable to continuous processes which attain a new steady state after a change in manipulated inputs within an acceptable time interval.

With *unsteady-state* (*dynamic*) *optimization*, the objective is not only to maintain a process at an optimum level under steady-state conditions, but also to seek the best path for its transition from one steady state to another. The optimality function then becomes a time function, and the objective is to maximize or minimize the time averaged performance criterion. Although similar to steady-state optimization in some respects, dynamic optimization is more elaborate because it involves a time averaged function rather than individual quantities.

The goal of control in this case is to select at any instant of time a set of manipulated variables that will cause the controlled system to behave in an optimum manner in the face of any set of disturbances. Usually, an *optimum behaviour* is defined as a set of output variables ensuring the maximization of a certain "objective" or "return" function (see p. 135), or a change in the output variables over a definite time interval such that a predetermined functional of these output variables is maximized or minimized.

As an illustration, we shall use the concept of a *phase space*. In a phase space, the states of a system are represented as points. In the general case,

with an arbitrary number n of output variables the phase space is depicted as an n-dimensional space which evades any graphical interpretation if there are more than three variables. With $n = 2$, the phase space reduces to a phase plane, and the state of the system can readily be visualized (Fig. I-27). With two output variables, y_1^0 and y_2^0, the state of the system will be represented by a point, y^0.

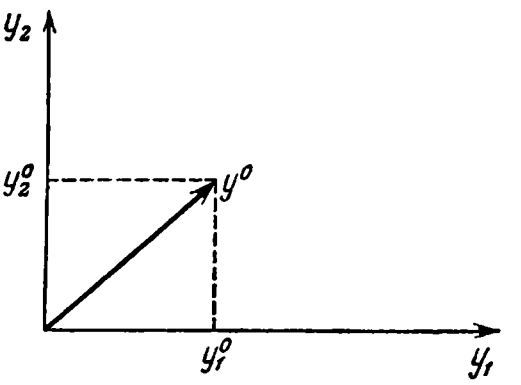


Fig. I-27. Phase plane

As a way of facilitating analysis, the variables of the system are written in vector form. The vector Y for which the coordinates are defined by a set of output variables $y_1, y_2, \ldots, y_n$ describes the state of the system:

$$Y = (y_1, y_2, \ldots, y_n) \tag{I-75}$$

while disturbances and manipulated variables are represented as

$$\xi = (\xi_1, \xi_2, \ldots, \xi_m) \tag{I-76}$$
$$U = (U_1, U_2, \ldots, U_r)$$

It should be stressed from the outset that in the general case the vectors Y, ξ, and U will have different dimensions, that is, the numbers n, m and r are different. Accordingly, phase spaces differing in dimensions will be necessary to depict the vectors ξ and U.

Any change in the vectors ξ and U causes the controlled system to move to a new state. In the phase space, this transition is depicted as a move from the original point y^0 to a new point y^1 along a path called the *phase trajectory*, connecting the original and new points (Fig. I-28). A set of trajectories is referred to as a *phase portrait* of the dynamic system.

If we are not interested in the path from point y^0 to point y^1 and only seek to evaluate what is gained by the move from the initial to the final state, we specify a certain objective function which is only a function of the state of the controlled system. If, on the other hand, we are interested in the path from the initial to the final state as well, we specify a functional of the trajectory and seek to choose this trajectory so as to minimize or maximize this functional. In an elementary case, this functional may be the time for a transition of the system from the initial to the final state, which is usually minimized.

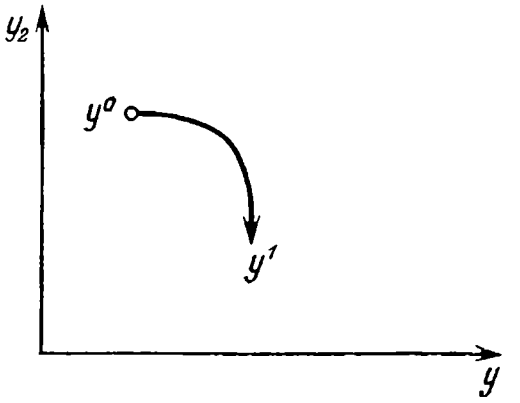


Fig. I-28. Phase trajectory

In the former case, resort is made to mathematical programming, and in the latter case, to calculus of variations, dynamic programming and the principle of maximality (see p. 158).

Dynamic optimization is applicable to start-up and loading operations and to processes having a large time constant and subject to changes in the variables that can be determined in advance.

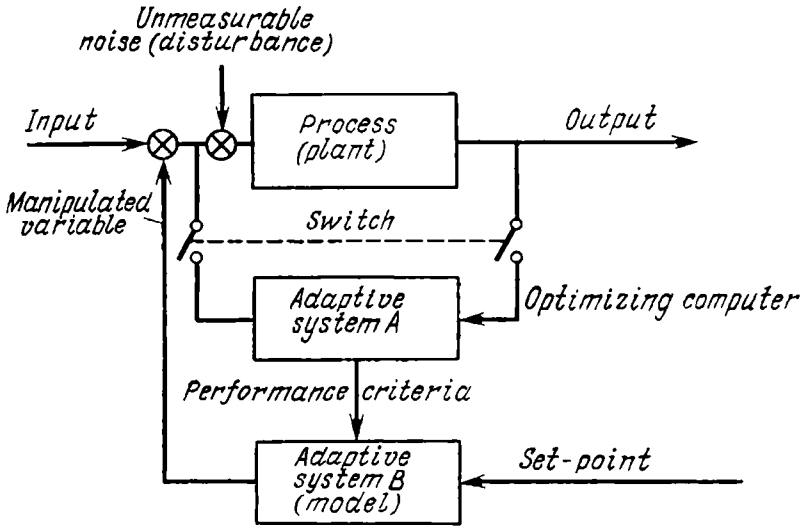


Fig. I-29. Optimizing control system with model adaptation

Another application for static and dynamic optimization is its use in conjunction with *model adaptation* (Fig. I-29). In this case, a mathematical description is derived statistically from observed input-output relations. The parameters of the model are estimated anew after each measurement of the selected output variable, using the regression analysis technique. In this way, each estimation is based on the most recent information describing the state of the process.

Adaptation of the model to uncontrollable external disturbances is secured by assigning probabilistic weights to these computations (for example, a probability of unity is assigned to the latest computations, and a probability of zero to the previous computations). This is accomplished by an optimizing loop in which the performance data are continually updated to yield appropriate parameter corrections or corrections are applied in the form of a data aging coefficient after each measurement.

The probability of error is evaluated in terms of the so-called certainty factor defined as

$$\beta = 1 - (s_R/s_E)^2 \qquad \text{(I-77)}$$

where s_R and s_E are the standard deviations of the manipulated variable

at the model output and input, derived from

$$s_R^2 = \frac{\sum_{i=1}^{\alpha} (u_i - u_i^*)^2}{\alpha - 1}$$
$$s_E^2 = \frac{\sum_{i=1}^{\alpha} (u_i - \bar{u}_i)^2}{\alpha - 1} \qquad \text{(I-78)}$$

where $\bar{u}_i$ is the mean of the manipulated variables, u_i^* is the model value of the manipulated variables and u_i is the true value of the manipulated variables.

Technical and economic analysis has shown that the use of optimizing computer control is justified in manufactures where the cost of the finished product exceeds the capital outlays for a computer control system by a factor of 15, and the pay-off period is within 24 months. If, after the installation of an optimizing control system, the economic gain is about 6%, this is an indication of a poorly managed process.

Self-adjusting control systems. These systems may be divided into three broad classes as follows:

(1) *Extremal control systems* which search for, and maintain, a maximum or minimum value for a performance criterion.

(2) *Self-adjusting systems* proper which modify controller (or system) parameters such as gain, derivative or integral time constants, feedback factors, or filter time constants automatically and in an unpredetermined manner.

(3) *Self-organizing systems* which modify the controller configuration to achieve self-adjustment or some other objective.

A classification of self-adjusting control systems is given in Fig. I-30.

Adaptive and learning control systems. These systems are recent important additions to automatic control.

Adaptive systems are those in which parameters, configuration and control actions are modified on the basis of the most recent information in order to force a "best" fit to the optimum system behaviour in spite of the initial uncertainty and under widely varying operating conditions.

Trainable control systems are those in which optimum output variables are generated in response to repetitively modified manipulated inputs and external performance corrections (repetitive computer control).

Learning systems differ from trainable systems in that no external performance corrections are applied.

In a way, adaptive systems may be looked upon as an outcome of work on optimizing and self-adjusting control systems and also as an alternative to conventional control.

Conventional analog control cannot optimize a process because the process variables change with time (that is, the mathematical model of the process changes), while the controller settings remain unchanged and, therefore,

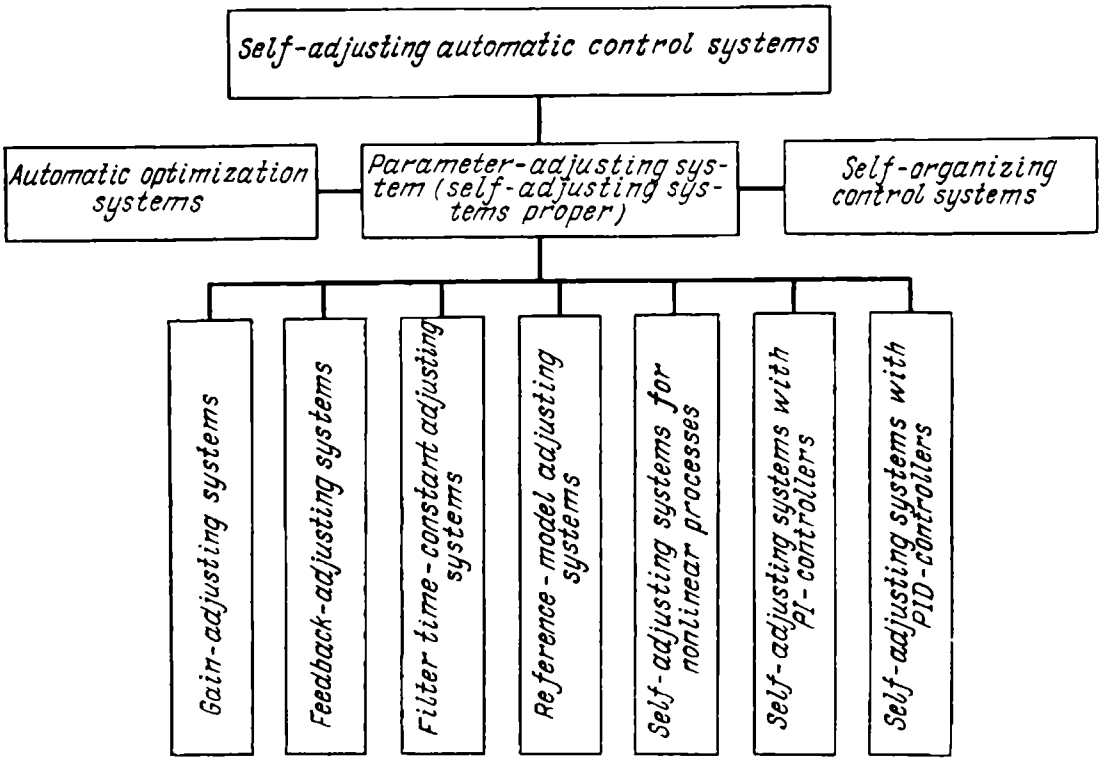


Fig. I-30. Classification of self-adjusting control systems

not optimal. Adjustment of controller settings by a self-adjusting control system is inefficient because a fairly lengthy system analysis would be inevitable. It is seen that the best choice is an adaptive system which forces a "best" fit to the optimum behaviour on the basis of the most recent information about the process and under widely varying operating conditions.

A classification of adaptive systems appears in Fig. I-31. In schematic form, an adaptive system is shown in Fig. I-32, and its flow diagram is in Fig. I-33.

With adaptive control, it is vitally important that the model be an adequate representation of the process. However, since the process variables change markedly with time, the switching instant predicted by the fixed-parameter model will be in error, and the transient response of the process will be anything but optimal. To counteract this development, it is important to monitor process variables continuously and to adapt the model as continuously in order to force an optimum fit of the model to the observed system behaviour in the vicinity of the operating point. The type of model used depends on the manner in which the process variables may change.

In chemical engineering, adaptive control is mainly realized through the use of optimizing facilities.

Reliability of control systems. The synthesis of control systems for chemical engineering is inseparable from the problem of control system reliability. The point is that system synthesis has to reconcile two conflicting trends.

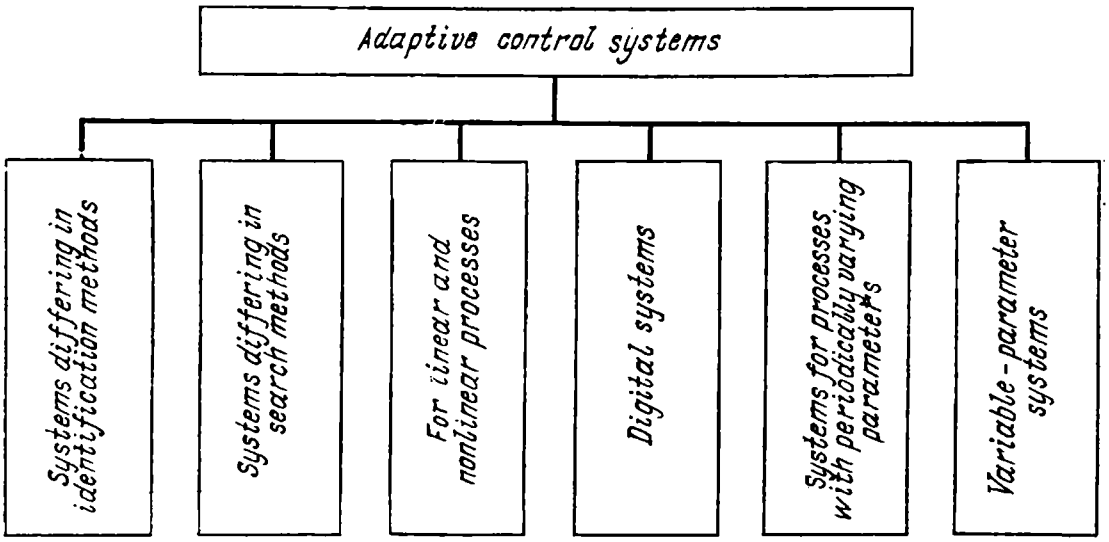

Adaptive control systems
Systems differing in identification methods
Systems differing in search methods
For linear and nonlinear processes
Digital systems
Systems for processes with periodically varying parameters
Variable-parameter systems

Fig. I-31. Classification of adaptive control systems

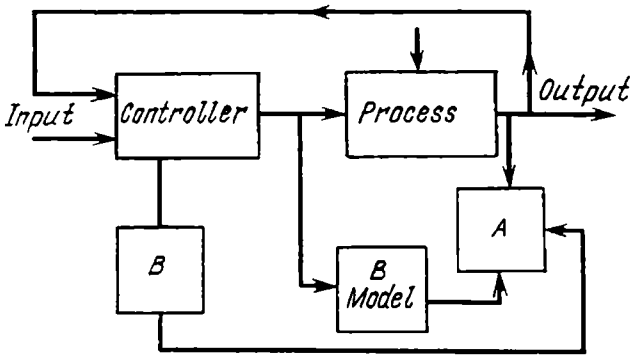


Fig. I-32. Block-diagram of an adaptive control system

A — quality performance computer; *B* — optimizing computer

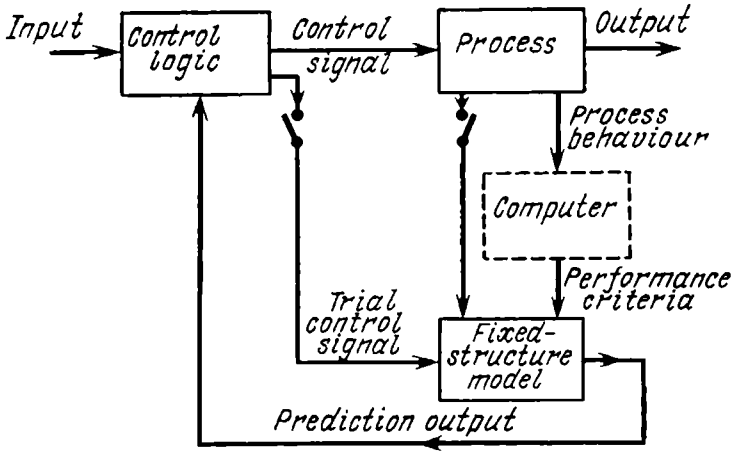


Fig. I-33. Block-diagram of an adaptive control system

On the one hand, the progressive increase in process or plant output and the use of integrated automation necessitate further improvements in control system reliability because even a minor failure would entail a sizeable economic loss. The reduction in attending personnel also acts in the same direction.

On the other hand, the range of functions that a control system is to perform is growing continuously, and so is the number of elements used to mechanize them, which inevitably tends to impair the reliability already attained.

The requirements that a reliable control system should satisfy may be stated as follows:

(1) The number of failures of critical elements (those whose failure would cause system shut-down) should be kept to a minimum.

(2) Facilities should be provided to locate and correct a malfunction as soon as it appears, or to alert attending personnel as to the presence and location of, and a remedy for, a trouble.

(3) The system should be constructed so that its components can be serviced independently (this can be done by system sectionalization or through the use of redundancy).

Improvements in reliability have been sought in three directions:

(1) System reliability –overall reliability of a complex device composed of elements connected in various ways.

(2) Component reliability—study into the physical properties of components.

(3) Reliability of signal transmission under conditions of noise (search for, and use of, noise-immune codes).

The search for, and the development of, novel principles for the synthesis of components employed in automatic control systems provides a basis for further advances in this field (improved sensitivity, higher stability, and faster response in conjunction with desired reliability, drastic reduction in power drain and size). An increasingly greater emphasis has been placed on the "building-block" principle with which any desired configuration of a control component or system can be built from a limited number of standard units without any further design or engineering work.

A good deal of interest is evoked by work on instruments which depend for their operation on the measurement of, or conversion to, frequency. Frequency can readily be measured to a high degree of accuracy, and a frequency signal can be transmitted with practically no distortion. Using frequency division multiplex, a large number of high-frequency signals from many instruments can be transmitted over a single coaxial cable. In other words, no ramified cable system is any longer necessary, while the measuring instruments can readily be modified in design and number without the need to change the cable.

(C) MANAGEMENT INFORMATION CONTROL SYSTEM (MICS)

At the top of the control hierarchy in the chemical industry stands a management information control system (MICS).

The objectives of such a system are: (a) centralized data acquisition; (b) data processing for performance evaluation and timely decision making; (c) indication and recording of off-normal conditions; (d) process optimization; (e) cost finding and accounting; (f) supply of information for management.

A management information control system is made up of a number of control and controlled subsystems interconnected by information (or communication) channels. Each control subsystem generates and feeds to the associated controlled subsystems the tasks that they should perform as part of an overall production process. Before a task is executed, each controlled subsystem will usually process appropriate information and take decisions as to the use of plant, source materials, manpower, specific production schemes, and the like. The extent, quality and speed of execution will usually be affected by the subsystem behaviour and by random external disturbances. Using feedback paths, the controlled subsystem will report back on the execution of the incoming commands and its status. On the basis of these back-reports and data coming in from other control and controlled subsystems, or other sources of information, each control subsystem takes new decisions on the execution of the production process.

All the subsystems of a management information control system are usually depicted on an *informational-functional model* which is the factory's informational diagram showing all the interrelations between the factory and external organizations, between the various departments within the factory and even between the key executives or employees. It also shows what information is exchanged (monthly plans, output per day, source materials expended over a month by a particular department and the like), in what form (programs, letters, verbal or written orders, summary reports on production or stocks and stores), at what intervals (daily, monthly, quarterly, annually, on demand), how it is processed, and how decisions are taken. This model gives a visual display of existing control loops and depicts all managerial activity. Since such a model might be overcrowded with detail, it is customary to break it up into a group of models.

These models may be classed in several ways. One is according to the degree of information detail. For example, an overall scheme of information flows may be constructed on the basis of generalized blocks which are then explained by a system of specialized models. As an alternative, models can be differentiated on a functional basis, that is, separate models may be used for information loops which handle supply of source materials, production planning, plant utilization, etc. As a further alternative, the models may be differentiated according to the time intervals at which they process and exchange information.

The pivotal objective for a management information control system is *to find an optimum production program under conditions of limited production resources or facilities.* The solution of this problem involves the use of a mathematical model representing the system behaviour, inventory levels, the state of physical facilities, and sales. As a rule, a factory operates under conditions of a limited supply of source materials, including those on hand or expected to come in during the planned period, by supply of packaging material (crates, cartons, etc.) made locally or purchased from outside suppliers, by the service life of plant, and by supply of labour.

The objective of a management information control system is then to turn out a production program (stating which quantity of each product is to be produced by which equipment and to what time schedule over a period in question) which would, when fulfilled, maximize the factory's profit. As a rule, this reduces to constructing a model as a system of linear inequalities such as shown below:[17]

$$\alpha = \begin{cases} \tilde{Y}^p x \leqslant \tilde{y}^{avail} \\ \tilde{U} x \leqslant \tilde{u}^{avail} \\ \tilde{V} x \leqslant \tilde{v}^{avail} \\ \tilde{T} x \leqslant \tilde{t}^{avail} \\ x^{gp} \leqslant \tilde{E}^g x \\ x^{bp} \leqslant \tilde{E}^b x \leqslant x^{bm} \\ c^p \leqslant \tilde{C}^T x \\ 0 \leqslant x \end{cases} \qquad \text{(I-79)}$$

$$p(x) = \tilde{P}^T x$$

The optimization problem may be formulated as follows: find x_{opt} yielding α such that $p(x_{opt}) = \max p(x)$ for all x's for which the condition α is satisfied. One of the key components of the model is the production program vector x; the components x_d (where $d = 1, \ldots, l$) carry information about the product obtained in the dth production cycle. Source materials should be consumed according to the planned consumption limits presented by the $\tilde{\tilde{Y}}^p$ matrix the $\tilde{y}^p_{jd}$ elements of which are equal to the amount of the jth source material ($j = 1, \ldots, m$) required to make one tonne of product in the dth production cycle.

The elements of the $\tilde{\tilde{Y}}^p$ matrix are computed through the use of mathematical statistics and digital computers. The starting data for computation are information about the amount of feed stock charged into and the amount of product discharged from a reactor, as stated in the respective process chart. Quotas for the consumption of packing materials are likewise presented in matrix form: the $\tilde{\tilde{u}}_{kd}$ elements of the $\tilde{\tilde{U}}$ matrix represent the amount of packing material of the kth form required to pack one tonne of product

manufactured during the dth production cycle ($k = 1, \ldots, k_n$). The labour requirements can be determined by means of the specific labour matrix $\tilde{V}$. Its elements, $\tilde{v}_{fd}$ ($f = 1, \ldots, f_n$) are equal to the time (in man-hours) expended by the fth group of direct labour to manufacture one tonne of product during the dth production cycle. These elements are found by statistically processing the daily performance records.

As regards the equipment utilization matrix, T, its elements, $\tilde{t}_{qd}$ ($q = 1, \ldots, q_n$) define the time (in reactor-hours) during which a reactor of the qth group is utilized in order to turn out one tonne of product in the dth production cycle. In determining these elements, it should be remembered that the reactors of the qth group in this production cycle may turn out either the finished product, or a semi-finished product, or both. Accordingly, the elements may be computed in four different ways as follows:

(1) $\tilde{t}_{qd} = 0$ if the dth production cycle is not performed by the reactors of the qth group;

(2) $\tilde{t}_{qd} = \tilde{\tau}_{qd}$ where $\tilde{\tau}_{qd}$ is the time required to turn out one tonne of finished product by a reactor in the qth group during the dth production cycle;

(3) $\tilde{t}_{qd} = \beta_d \tilde{\tau}^{\beta}_{qd}$ where $\tilde{\tau}^{\beta}_{qd}$ is the time required to manufacture one tonne of semi-finished product by a reactor of the qth group during the dth production cycle, and β_d is the amount of this semi-finished product required to make one unit of finished product;

(4) $\tilde{t}_{qd} = \tilde{\tau}_{qd} + \beta_d \tilde{\tau}^{\beta}_{qd}$.

The values of $\tilde{\tau}_{qd}$ and $\tilde{\tau}^{\beta}_{qd}$ are found from process charts, using mathematical statistics and digital computers, while the values of β_d are taken from the respective time schedules. Use is also made of the product price vector $\tilde{C}$ and the (planned) profit vector $\tilde{P}$ per tonne of product sold. For proper planning and accounting, it is important also to know the amounts of product of the various brands and groups. In order to go over from the production program vector to the product brand vector, use is made of the E^b matrix whose elements $\tilde{e}^b_{id} = 1$ if the ith brand of product is manufactured, and $\tilde{e}^b_{id} = 0$ if the ith brand of product is not manufactured, during the dth production cycle. Similarly, use is made of the E^g matrix in going over from the production program vector to the product group vector.

A separate group comprises model elements which represent the factory's inventories. These are the raw material inventory vector $\tilde{y}^{avail}$, the packing inventory vector $\tilde{u}^{avail}$, the available labour force (man-hour) vector $\tilde{v}^{avail}$, and the available reactor-hour vector, $\tilde{t}^{avail}$.

A special group includes constraints related to planning and sales. These are the planned brand output vector x^{bp}, the planned group output vector x^{gp}, the planned value for marketed products c^p, and the marketing forecast vector x^{bm}.

Using the above designations, it is seen from the formalized statement of the problem that the objective is to optimize the performance of the department under conditions of limited production resources and facilities; the

optimality criterion is the maximum profit. Besides, the left-hand side of the model may be used to find the amounts of source materials, packing material, labour force, and equipment operating time needed to realize the sought production program, and also output in terms of products of the various brands and groups, the cost of the marketed products, and the profit that can be cleared from sales. The optimization problem is solved on a digital computer, by the simplex method.

Optimizing planning and control is accomplished for different time intervals and has an hierarchic time structure. In the first stage, an optimum annual program, $x_{opt}(Y)$ is determined, using linear programming. Since the factory is interested in fulfilling the production program, all of its indices are found by multiplying the vector $x_{opt}(Y)$ by the respective matrices and vectors, source and packing materials are ordered, and so on. The yearly plan is broken down into quartery plans in proportion to the number of working days in each. The selected program is a tentative one because all constraints have been made with a large measure of uncertainty. Therefore, it is continually corrected as more accurate data become available.

Physically, a management information control system is realized by local optimizing, regulatory, indication, switching and remote control systems.

Information about the progress of the process comes in from the various plant units via transducers, T, and converters, C (Fig. I-34) to scanners used as local input devices which normalize the signals coming from the various transducers and pass the data on to a central data logger in the central control room.

With existing local control systems, data monitoring and logging equipment and computers, centralized process control is no problem.

The data logger records performance outputs at predetermined intervals, compares them with set-point values, generates off-normal limit signals when appropriate, records off-limit values, and feeds signals to an optimizing computer and to the factory's central control room. The optimizing computer computes optimum set-point values for the various production areas, using equations built into its program, and also performs mathematical and logical operations to determine what corrections should be applied to controller settings.

On the strength of these computations and also on the basis of progress reports from the production areas, the duty production engineer takes appropriate decisions and notifies the respective area operator via a command distributor, about the changes that should be made in the process conditions. In response, the area operator adjusts the controller settings and final control elements as ordered.

In addition to the functions described above, the computer can keep an inventory of raw materials and finished products, and carry out research involving the measurement of process characteristics, accumulation of statistical data, and determination of mathematical relationships between process variables in order to work out control algorithms. Optimum opera-

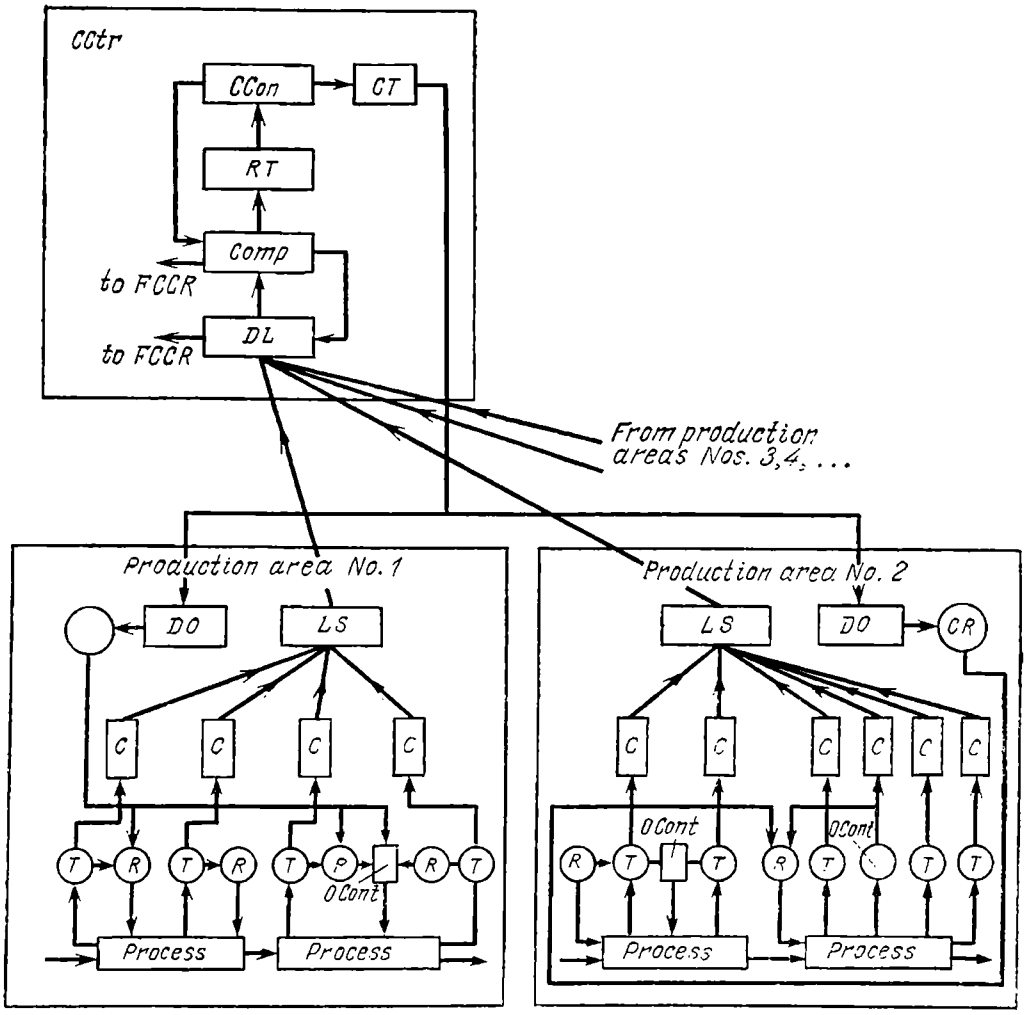


Fig. I-34. Process data logging and control system

CT - command transmitter; *CR* — command receiver; *RT* — recommendation transmitter; *Comp* — optimizing computer; *T* - transducer; *DO* — duty operator; *DL* — data logger; *LS* — local scanner; *OCont* — optimizing controller; C - converter; *CCon* — control console; *R* — regulator; FCCR — factory central control room; CCtr — control centre

ting guides are derived from the information supplied by the process(es) and the control algorithm built into the computer.

Further requirements for a centralized factory control system may be stated as follows: the system should be sufficiently reliable (a temporary trouble in some elements ought not to cause failure of the entire system), use standard elements, have a sufficiently high scanning rate, ample storage capacity, sufficient data processing rate, and display end data faithfully.

Thus, a management information control system takes in information from all the lower levels in the hierarchy, that is, from the local control systems at the reactor and unit-operation level and also from the process control systems at the departmental level.

I-9. COMPUTERS AS TOOLS OF CYBERNETICS

Mathematical models of processes are constructed and tested for the purpose of process and control optimization with computers. As cybernetical devices, computers perform three distinct functions, namely: (1) carry out computations, (2) simulate processes and (3) control processes.

There are two major classes of computers, analog and digital.

(A) ANALOG COMPUTERS

An analog computer operates by setting up an analogy between a real process and its mathematical formulation.[18-22]

As has already been shown (see p. 16), the same differential equations can be set up to describe widely varying processes, such as viscous friction, thermal conduction, diffusion, electric current, etc. On this basis it has been pointed out that the mathematical models of different processes are isomorphic. Practically, this implies that by using this type of analogy, equations describing physical and chemical processes can be solved as those applying to electric phenomena. In this sense, a process taking place in a chemical reactor is simulated, that is represented by its electrical analogy, on an analog computer. Through such simulation on an analog computer, we can readily obtain the information we need about the process and the associated reactor as if we operated them in reality.

In an analog computer, the variables of the differential equation describing the process being simulated (machine variables) are expressed in units of voltage (volts), and the independent variable in units of time, because the machine variables are integrated with respect to time.

Analog computers do not operate on or display numbers; their outputs take the form of continuously varying voltages which are displayed by instruments or on oscilloscopes.

Design of an analog computer. An analog computer is a collection of computing elements performing various mathematical operations on machine variables. The computing elements needed are summarized in a block-diagram which shows how the various blocks are to be interconnected. Then scale factors are selected to relate each dependent and independent variable of the prototype system with a corresponding variable in the computer. A detailed set-up diagram is then drawn, showing the detailed patch board connections of all computing elements. Finally the computer is programmed as indicated by the set-up diagram so that the final set-up will obey the equation (in electrical form) being solved. The data comprising the solution are obtained and recorded as time functions of the voltages representing the input variables on the scale specified for the independent variable. Operations on machine variables are carried out simultaneously and continuously by all computing elements.

The heart of an analog computer is a high-gain d.c. operational amplifier (Fig. I-35) with feedback $[z(p)_0]$ and an input circuit $[z(p)_1]$, capable of sign

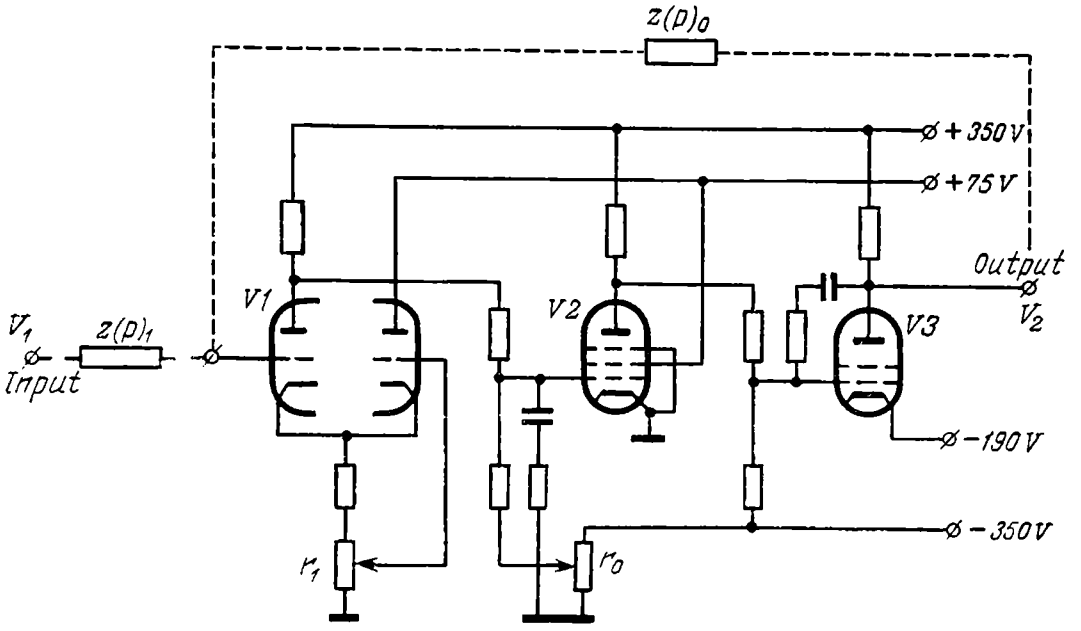


Fig. I-35. Circuit of a three-stage d.c. operational amplifier

$z(p)_0$ — feedback impedance; $z(p)_1$ — input impedance; $V1$ — 6H9C dual triode; $V2$ — 6Ж8 pentode; $V3$ — 6П6С beam tetrode; V_1, V_2 — input and output voltage. Resistor r_1 is adjusted to minimize drift in output voltage; resistor r_0 is adjusted to set output voltage to zero (zero setting)

inversion. Here $z(p)$ designates the impedance of the respective circuit in operational notation.

In the general case, the mathematical operation performed by a d.c. operational amplifier has the form

$$z(p)_0/z(p)_1$$

If both circuits are pure resistances, R_0 and R_1, respectively, then by Kirchhoff's first law for the point g we have:

$$V_2 = -V_1 \cdot \frac{R_0}{R_1}$$

The d.c. operational amplifier answering this relation multiplies the machine variable by a constant.

With three resistances connected to the amplifier input, Kirchhoff's first law gives

$$V = -\left(V_1 \frac{R_0}{R_1} + V_2 \frac{R_0}{R_2} + V_3 \frac{R_0}{R_3}\right)$$

where V is the output voltage. This operation is summation, and the device performing it is called a summer.

Placing a capacitor C in the feedback path and a pure resistance at the input turns the d.c. operational amplifier into a device performing integra-

tion, which is the basic operation in the solution of differential equations:

$$V_2 = -K \int_0^{\tau} V_1 \, d\tau$$

where $K = 1/RC$, and R is the input impedance. The respective device is called an integrator.

The symbols used for the above and other analog computer units are listed in Table I-12.

The MH-7 analog computer. This is a typical Soviet-made computer. It has 16 operational amplifiers of which six may be used as integrators, two as differentiators, and each can be connected as a summator, a scaler, or a sign inverter. The machine also has four nonlinear computer units and a patchboard for interconnecting the computer units as may be required.

All variables in the computer are represented as d.c. voltages in the range ± 100 V. Because of this, the multiplier (see Table I-12) uses a scale factor of 0.01. Since the maximum value of the variables being multiplied may be as high as 100 V, a scale factor of 0.01 ensures that the product will never exceed 100 V. The computer solution is displayed on an oscilloscope or, if the process is slow, by pointer instruments. Besides, the machine can be halted at any instant to measure the various quantities.

The "MH-7" can solve ordinary linear and nonlinear differential equations up to the sixth order inclusive or systems of six simultaneous first-order equations. The computer can readily be ganged up with a similar machine or machines, so that the order of the equations that can be solved is raised in proportion.

General steps in the solution of problems on an analog computer. As already noted, an analog computer solves differential equations which describe the process in question. Before these equations can be set up on the computer, the following preliminary steps are carried out.

(1) A block-diagram is drawn up. It summarizes the computer elements needed to perform the specified mathematical operations and indicates how the various elements are to be connected.

(2) Scale factors are selected. These factors relate each dependent and independent variables of the process with a corresponding variable in the computer.

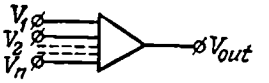
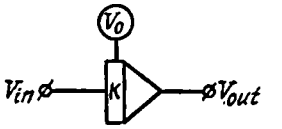
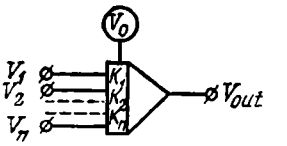
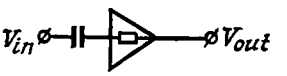
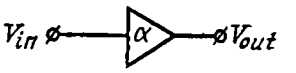
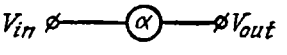
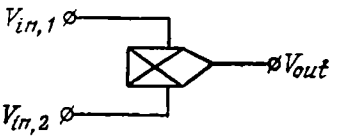
(3) The model parameters are estimated from the coefficients of the original equations and the selected scale factors.

(4) The initial conditions and excitations for the model are determined in terms of the physical quantities which represent the original variables of the problem in the computer.

A *block-diagram* for computer solution is drawn up by reducing the mathematical operations specified by the original mathematical model (equations) to those that can be handled by the computer, that is, integration, summation, sign inversion, and function generation.

Table I-12

Analog Computer Operations and Diagram Notation

Device	Operation	Symbol
Summer	$V_{out} = -(a_1V_1 + a_2V_2 + \ldots + a_nV_n)$ $= -\sum_i^n a_i V_{in,i}$	
Integrator	$V_{out} = -K\int_0^\tau V_{in}\,d\tau + V_0$, where $K = 1/RC$ R = input resistance C = feedback capacitor V_0 = initial condition	
Summing integrator	$V_{out} = V_0 - \sum_i^n K_i \int_0^\tau V_{in,i}\,d\tau$ $K_i = 1/R_iC$	
Differentiator	$V_{out} = -K\frac{dV_{in}}{d\tau}$	
Scaler	Multiplication by a constant: $V_{out} = -\alpha V_{in}$	
Sign inverter	Sign inversion: $V_{out} = -V_{in}$	
Potentiometer	Multiplication by a constant without sign inversion: $V_{out} = \alpha V_{in}$ $0 \leqslant \alpha \leqslant 1$	
Multiplier	$V_{out} = 0.01\,V_{in,1} \times V_{in,2}$	
Function generator	Reproduction of nonlinear functions: $V_{out} = f(V_{in})$	

Each equation is solved for the respective highest order derivative which is repeatedly integrated by a cascade of integrators until the sought variable appears at the cascade output.

According to the arrangement of the equation resolved for the highest order derivative, the summator yields the true value of the highest order derivative. Since the summator changes the sign of the voltage, the sum appears to have been multiplied by minus unity. After integration, the terms of the equation will also have been multiplied by minus unity.

Examples of block-diagrams developed for computer solution of differential equations follow.

Example I-5. Draw up a block-diagram for the solution of a differential equation with known initial conditions:

$$d^2x/d\tau^2+x = 0$$
$$x(0) = a \quad x'(0) = b$$

Re-arranging the equation to solve for the highest order derivative, we get

$$d^2x/d\tau^2 = -x$$

The number of integrators is the same as the order of the equation being solved. Therefore, we need two integrators. In accordance with the equation at hand, to generate the highest order derivative, the value of the sought function should be taken with the opposite sign; this can be done by one sign inverter (Fig. I-36).

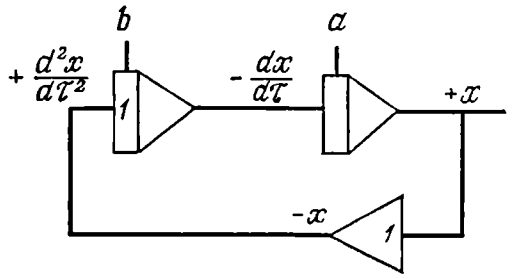


Fig. I-36. Problem set-up (to Example I-5)

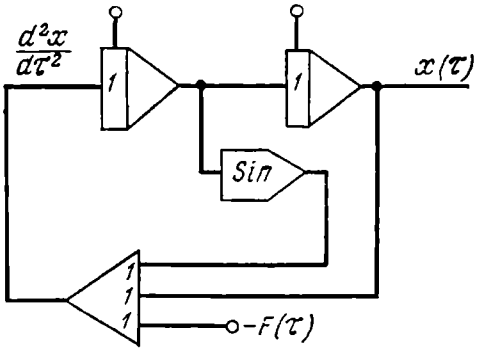


Fig. I-37. Problem set-up (to Example I-6)

Example I-6. Draw up a block-diagram for the computer solution of a nonlinear differential equation with known initial conditions:

$$d^2x/d\tau^2+\sin dx/d\tau+x = F(\tau)$$

On rearranging the equation to solve for the highest order derivative, we have

$$d^2x/d\tau^2 = F(\tau)-x-\sin dx/d\tau$$

As is seen, we need two integrators to obtain the sought function and one function generator for sin $(dx/d\tau)$. The excitation $F(\tau)$ may be either provided by a special generator or reproduced by some computer units. One summator is needed to obtain the sum of the terms on the right-hand side of the equation. The resultant diagram appears in Fig. I-37.

Scale factors relating each dependent and independent variable of the prototype system with a corresponding variable in the computer are selected on the basis of actual knowledge of the process, taking the necessary steps to minimize the error in the final solution. This is usually done by firstly guessing, then revising and improving the highest values for the voltages on each computing element in the course of computer solution.

The independent variable of an analog computer is time. The time scale is chosen according to the statement of the problem and the requirements for optimum operation of the model. Analog computers can operate in real, scaled-down or scaled-up time.

All physical quantities entering the system of differential equations are represented by voltages multiplied by suitable scale factors. If x is a dependent variable and V_x is its representation or analog in the computer, then using a scale factor, N_x, we get

$$x = N_x V_x$$

As often as not, the variables of the prototype system are measured in relative units, X, varying in the range $0-1$. Then, the effective range of analog voltages (usually from 0 to ± 100 V) may conveniently be represented as the *machine unit* range from 0 to ± 1 (that is, 100 V = 1 machine unit). In such a case, all scale factors will be unity, which is convenient in determining the gains of the individual computing elements, especially in solving nonlinear differential equations. Since the upper and lower limits upon the excursions of process or system parameters are not always known precisely at the formulation of the problem, it is usual to revise and improve scale factors in the course of computer solution.

All the subsequent steps of problem solution and simulation on an analog computer will be clear from the example that follows.

Example I-7. Let a complex reaction go on in a constant-temperature batch-type reactor, such that the rates of the constituent simple reactions correspond to stoichiometric ratios:

$$A+B \xrightarrow{k_1} 2R \qquad w_{r1} = k_1 C_A C_B$$

$$B+R \xrightarrow{k_2} 3S \qquad w_{r2} = k_2 C_B C_R$$

where A and B are the reactants, R and S are the reaction products, w_{r1} and w_{r2} are the reaction rates, k_1 and k_2 are the reaction rate constants, C_A, C_B and C_R are the respective concentrations.

The respective differential equations may be written as follows:

$$\frac{dC_A}{d\tau} = -k_1 C_A C_B \qquad \frac{dC_B}{d\tau} = -k_1 C_A C_B - k_2 C_B C_R$$

$$\frac{dC_R}{d\tau} = 2k_1 C_A C_B - k_2 C_B C_R \qquad \frac{dCS}{d\tau} = 3k_2 C_B C_R$$

The variables of the kinetic equations may be expressed in terms of voltages as follows (τ_M is the machine time):

$$\frac{dV_A}{d\tau_M} = \alpha_1 V_A V_B \qquad \frac{dV_B}{d\tau_M} = -\alpha_2 V_A V_B - \alpha_3 V_B V_R$$

$$\frac{dV_R}{d\tau_M} = \alpha_4 V_A V_B - \alpha_5 V_B V_R \qquad \frac{dV_S}{d\tau_M} = \alpha_6 V_B V_R$$

where

$$\alpha_1 = 100 k_1 N_{C_B} N_\tau \qquad \alpha_2 = 100 k_1 N_{C_A} N_\tau$$

$$\alpha_3 = 100 k_2 N_{C_B} N_\tau \qquad \alpha_4 = 2 \times 100 k_1 \frac{1}{N_{C_R}} N_{C_A} N_{C_B} N_\tau$$

$$\alpha_5 = 100 k_2 N_{C_B} N_\tau$$

$$\alpha_6 = 3 \times 100 k_2 \frac{1}{N_{C_B}} N_{C_B} N_{C_R} N_\tau$$

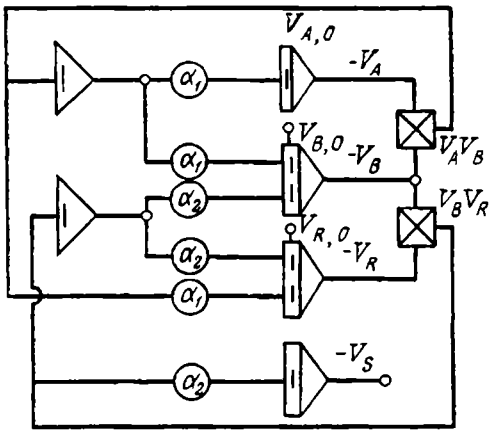


Fig. I-38. Problem set-up (to Example I-7)

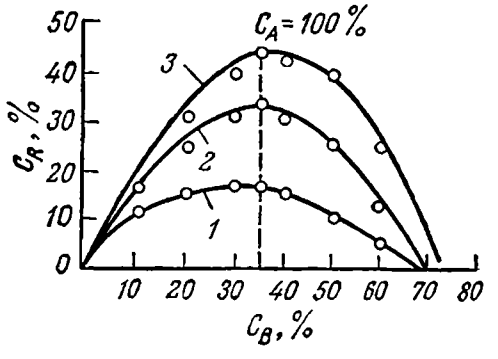


Fig. I-39. Yield curves for product R plotted on the basis of analog-computer data

1 – $k_1/k_2 = 0.5$; *2* – $k_1/k_2 = 1$; *3* – $k_1/k_2 = 2$

The set-up diagram for computer solution of the problem is shown in Fig. I-38. The initial conditions at $\tau_M = 0$ are $V_A = V_{A,0}$, $V_B = V_{B,0}$, $V_R = V_{R,0} = V_S = 0$.

We seek to find the concentrations of the reactants A and B and the reaction rate constants that will maximize the yield of the product R. The concentration of the sought product as a function of C_B can be found by varying the concentration of the reactant B, that is, by setting various values for $V_{B,0}$ or the voltage defining the initial conditions. The values of C_R are read on a voltmeter.

The curves relating the yield of the product R for three values of the ratio of reaction rate constants appear in Fig. I-39. The desired ratios k_1/k_2 are obtained by a selection of fixed or variable resistors on the patchboard of the computer. Referring to Fig. I-39,

at $C_B = 35\%$, C_R has a maximum which is independent of the ratio k_1/k_2. Thus, at $C_A = 100\%$ and $C_B = 35\%$, the reaction proceeds under optimum conditions as regards the product R.

(B) DIGITAL COMPUTERS

A digital computer may be described as a device which operates with information represented in digital form. In other words, it operates on numbers, and these may be handled by the rules of arithmetics and logic. The use of digital computers for problem solving is based on the fact that the solution of any problem may be represented as a sequence of elementary operations.

When he is solving a problem with pencil and paper, a human being does these elementary operations in a precisely definite sequence; any departure from this sequence would yield an erroneous result. Obviously, if a digital computer is instructed as to the order of operations, it will do them at a much faster rate, and the problem in question will be solved in a shorter time. With a digital computer, the sequence of operations is specified by a *program*, and the information to be operated upon is read or written into the computer as *data*.

In contrast to analog computers, both the program and the data for a digital computer are presented in digital form, that is, as numbers. On entering the computer, digital information is converted to a sequence of electric pulses, and all the subsequent computational operations are carried out on them.

As a rule, digital computers do not operate on numbers in decimal notation. Numbers in the machine are usually presented in binary notation which uses only two different digits, 0 and 1. Even though information may be set into a computer in a decimal code, it will subsequently be converted to a binary code. In digital computers, the binary number system has been preferred only because it is simple to mechanize.

A digital computer operates on data, or numbers, as directed by instructions. All available basic operations within a computer make up what is known as the *computer instruction set*. Since, however, a digital computer operates automatically, it must be told which instructions of the set are to be actually used and on which numbers. This is done in the form of a program. Both the program and the numbers are supplied to the computer in advance and, as a rule, separately. Then the same program can be used to solve problems with different numbers.

The program and the numbers are written on any one of several physical media (punched paper tape, punched cards) as combinations of perforations in, say, the international telegraph code, and loaded into the computer. Then the instructions of the program are executed, and the computer is caused to perform the corresponding basic operations. After the computations are completed, the result is printed or punched out, according to the form of presentation desired.

The efficiency of a digital computer as regards problem solving is above

all dependent on how fast it can perform the basic operations built into its hardware, and also on how large the blocks of numbers that can be operated upon at a time are. Accordingly, digital computers are classed on the basis of the speed of operation and the capacity available for the storage of numbers. The *speed of operation* is expressed as the number of operations performed per second, and the *storage capacity* as the number of storage locations allocated to the program and numbers. Each storage location or cell can store only one number or one instruction as a set of digits of standard length. Present-day digital computers have a speed running into millions of operations per second and a practically unlimited storage capacity.

All digital computers may be divided into two broad classes, namely general-purpose and special-purpose computers. *General-purpose computers* can handle a wide range of problems and usually have a large computer instruction set and a large storage capacity. *Special-purpose computers* are specifically designed to solve a narrow range of problems in a specific field of technology or under specific conditions.

The five basic functional units of a digital computer are a storage (or memory), an input device (or devices), an output device (or devices), an arithmetic unit, and a control unit. In schematic form, the relationships between them are shown in Fig. I-40, and a brief outline of each follows.

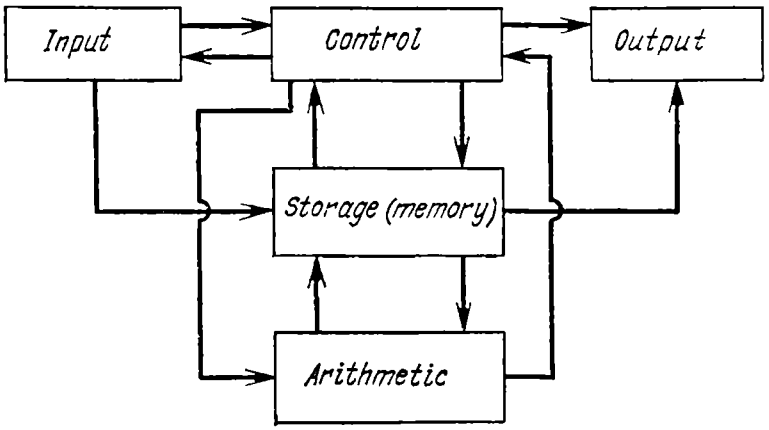


Fig. I-40. Block-diagram of a digital computer

Storage (memory) unit. The function of the storage or memory unit, as its name implies, is to store the program, data and intermediate results. Any word (which may be a number or an instruction) written into a particular storage location may be transferred in the course of problem solving to any other computer unit without destroying the contents of the previous location. The capacity of the storage unit is expressed as the number of storage locations. Each location is described in terms of bits or bit positions, and their number determines, in the final analysis, the accuracy of number presentation in the computer.

An important characteristic of the storage unit is the access time per word, which is defined as the time interval required to find a particular word in the storage and to transfer it to another unit. The access time has a direct bearing on the speed of the computer, because in executing a program both numbers and instructions are taken from the storage unit.

A large fast-access storage or memory is usually difficult to realize physically because of some limitations, such as the standard length of a word. This is why present-day digital computers use two types of storage, internal and external.

The principal internal (or working) storage has a fast access time and is continually used in computations. Its capacity is usually limited to a few thousand information units. In contrast, an external storage is much slower, but is more capacious (practically unlimited).

The difference in purpose and performance between the two types of storage has dictated the choice of physical media used. Most often, the internal storage uses magnetic cores (the core storage). These are bistable devices, one state being the positive residual magnetization designated as binary 1, and the other state being the negative residual magnetization designated as binary 0. Application of a pulsed current equal to the core saturation current will set the core in a desired binary state where it will remain until pulsed in the opposite sense. This change of polarity occurs in a negligible time interval.

Physically, a core storage location is built as follows. A group of cores corresponding to one word of information is threaded by wires which carry the write or read current. In addition, each core is threaded by write and read wires of its own. When a current equal to the core saturation current is applied to a core, it will change its state of residual magnetization, and a write pulse, if one is applied, will cause that core to store a 0 or a 1. In a similar way, the information stored can be read out by applying a zero write pulse. If a core has already been set to the 0 state, it will not change state, and no emf will be induced in the read wire. If, on the other hand, it has been set to the 1 state, such an emf will be induced.

External storage is usually built with magnetic tape, magnetic discs, or magnetic drums to which a coating of ferromagnetic oxide is applied. Information is written on or read from the ferromagnetic surface of a tape, drum or disc by write-read magnetic heads as the tape, drum or disc moves past the head. In writing, the head induces an emf in the ferromagnetic coating, thereby changing its magnetization appropriately (to represent a 0 or a 1); in reading, the head senses this state of magnetization, and the emf induced in the head is a representation of a 0 or a 1. The access time of such storage depends on the speed at which the medium passes past the heads and usually ranges from a few tens of milliseconds to several seconds.

During the solution of a problem, there is a continuous exchange of information between the internal and external storage units. As a rule, information is exchanged in large blocks of numbers.

Input unit. The function of the input unit is to supply numbers and

operating instructions (programs) to the machine. This is done by electromechanical devices operating at speeds which are by several orders of magnitude lower than that of other electronic units of the computer. Depending on the class of computer used, there may be off-line and on-line input devices. *Off-line input devices* operate independently of the other units of the machine and have, as a rule, storage units of their own. During an input operation, the information may be put into that storage, while the machine is free to perform any other operations. If and when necessary, the machine can withdraw the information it needs from this storage and proceed with computations. With an *on-line input device*, the device can only perform input operations during the input stage.

Irrespective of the organization of input equipment, it should be capable of accepting information represented by combinations of perforations on punched tape or punched cards and converting them to pulse sequences. With numerical information, the input device converts it from decimal to machine notation. Sometimes, the conversion from one number system to another is done to a predetermined program.

Output device. The function of an output device is to present intermediate or final results in a form convenient for further use. The presentation may be in binary or decimal notation, in the form of tables or charts. Output operations are performed by electromechanical devices, and their speed of operation is considerably lower than that of the computer proper. Accordingly, as is the case with input devices, output devices may be off-line or on-line.

Arithmetic unit. This unit performs the various operations on numbers in the computer, namely addition, subtraction, multiplication, division, etc., for which purpose it contains appropriate computing elements. It has a storage of its own, to store the numbers for the duration of the respective operation. Such a storage device is called a register and has a capacity for one word. Typically, an arithmetic unit has three to five registers. The contents of the registers are displayed on the control console.

A complete operating cycle of the arithmetic unit is as follows: (a) information is transferred from the storage unit to the registers; (b) arithmetic operations are performed; (c) the results are transferred to the storage unit.

Control unit. The function of the control unit is the interpretation of instructions in accordance with the program. A program is the schedule of instructions defining the order in which the programmed instructions should be executed. When an instruction is received in the control unit, that unit must provide the signals, usually as trains of pulses, that will cause the respective unit of the computer to perform the needed operation. If, for example, this is an arithmetic instruction, the control unit will cause the requisite operands to be fetched from the storage unit, the arithmetic unit to perform the specified operation, and the result to be transferred to the storage unit.

Programming. Digital computers can only perform a limited number of

basic operations defined by the computer instruction set. Therefore, any complex operation must be reduced to a chain of simpler ones which are within the computer's ability. The process of reducing complex operations to simpler ones and preparing a set of coded instructions for the computer to perform the individual operations in order to obtain the final solution is called *programming* and the set or schedule of instructions is called a *program.*

Programming may be hand or automatic.

With *hand programming*, a programmer maps an external problem into the logical structure of a digital computer by preparing a list of instructions, or program, step by step, to be performed in sequence by the computer. That is, all instructions are written directly in terms of the computer's basic set. If, say, the generation of a trigonometric function is not a basic operation for a particular computer, the programmer should replace it with operations of addition, subtraction or multiplication. This is why a programmer trained to compile programs for a given class of digital computers may fail to do so for other classes. For the same reason, a program written for one computer may be unfit for another.

Although the control generally proceeds sequentially down the ordered list of instructions, under some conditions it may be necessary to depart from the ordered sequence and to go to an entirely different part of the program. If this departure is to be executed irrespective of conditions in the computer, this is an *unconditional transfer* or *jump*. In contrast, a *conditional transfer* or *branch* will occur only if a specified condition has been satisfied, for example, the number in a given location exceeds the number in the register of the arithmetic unit. The jump and branch instructions are the means by which the machine circles each loop of computation, that is, a sequence of operations cycled repeatedly and then escapes from the loop, or branches into a subroutine, that is, operations using alternative equations for the same computation.

With hand programming, errors are very likely to creep in, because the instructions only differ in numerical codes, and there are tens or even hundreds of such instructions in a program. This is why groups of instructions, each doing some specific job, are programmed once and placed in the storage unit. Such a self-contained group of instructions is called a *subroutine* (or routine). Examples of subroutines are those for the computation of elementary functions or for solving standard problems in computational mathematics. Subroutines are organized in subroutine libraries which are a valuable aid to any computer. When necessary, these subroutines may be included in a given specific program directly.

Programming in terms of machine commands presents a serious training problem, for one has to memorize the computer instruction set and the operation codes, and the resultant program in no way resembles a mathematical description of the problem. Besides, a hand program is difficult to de-bug, that is, it will most certainly contain some errors.

This is why increased emphasis has recently been placed on *automatic*

programming. In simple terms, automatic programming reduces to the following. The algorithm of a problem written in a suitable "programming" language and algebraic equations is transferred onto punched tape, and this is fed into the computer storage. Since the programming (or source) language differs from machine (or object) language, the necessary coding is done by translator or compiler programs placed in the computer storage in advance. All the remaining steps –the selection of a correct sequence for instructions and joining together the program parts—are then carried out by the computer which thus synthesizes a program or algorithm in terms of the machine language and stores it, if necessary.

As is seen, automatic programming necessitates the use of a programming language intelligible to both man and computer. Also, with multi-machine installations in which each machine has a separate language of its own, a unified programming language is important for most efficient use.

At present, the most commonly used automatic programming languages are ALGOL (short for Algorithmic Language) and FORTRAN (short for Formula Translation). These are universal programming languages. In fact, they provide a basis for an exchange of algorithms between programmers.

Basic steps in solving a problem on a digital computer. These steps, closely related to one another, are as follows:

(1) A mathematical description of the problem to be solved is prepared.

(2) A numerical method is chosen for solution (according to the accuracy desired and the machine time that may be expended) and an algorithm is synthesized.

(3) An appropriate program is compiled and de-bugged.

(4) The computer is run to solve the problem.

Setting up a mathematical description is probably the most important and challenging part in the computer control of industrial processes. Whether or not a particular mathematical description faithfully represents the prototype system or process depends on how intimately the latter is known. On the other hand, a mathematical description overcrowded with detail may lead to considerable computational difficulties unsurmountable even for large-capacity computers. This is why one has to have a clear idea of the computational limitations imposed by the equations used, already at the time of writing up a mathematical description. If a problem is to be solved for the first time and there is no past experience on which to draw, the next step is the selection of a numerical method.

The selection of a numerical method, too, depends on the nature of the problem being solved and, very often, on the capabilities of the available computer. For example, one cannot hope to solve a system of linear equations of the 100th order on a small computer by direct methods, because the coefficient matrix would be too large for the storage unit to hold or because the results would be low in accuracy. Thus, a detailed knowledge of numerical methods is a vital point in deciding whether a given computer can handle the problem at hand. On the other hand, the mathematical problem in a specific statement is an image of the physical nature of a process with all of

its peculiarities and limitations. A good knowledge of these peculiarities and limitations may greatly simplify the computational procedure without any loss of generality. For example, if it is known that the solution is a real number, all complex solutions may be discarded in advance through the use of logical operations.

After a particular numerical method has been chosen, comes the turn of algorithm synthesis. An *algorithm*, as the reader may have already construed, is a computing procedure or method for reaching the desired goal in a finite number of steps. Usually, an algorithm is presented as a *flow diagram*.

Now a program is compiled and de-bugged. It may be written either in terms of machine instructions or in terms of a programming (or source) language. The choice depends on the level of automation in programming. A program in a source language can be compiled faster and with fewer errors because a group of operations can be represented by a single symbol. However, programs compiled automatically operate at a slower rate than hand programs, which is a serious limitation if the computer has a relatively low operating speed. A program written in machine instructions is executed immediately after it is read into the machine, while a program written in terms of a source language must first be translated into the object (or machine) language.

Before a program can safely be used in actual computations, its behaviour must be thoroughly tested and proved to be correct. In the early years, the usual procedure was to run the program one instruction at a time and compare the intermediate and final results with those computed manually for de-bugging purposes. As often as not, however, a problem cannot be solved manually. This is why most modern installations are provided with special diagnostic programs which do the same job, but more accurately and at a higher speed. Depending on the nature of errors, the solution may be re-run, starting with the first or any other stage.

After the behaviour of the program has been proved to be correct, the problem is solved, using various sets of input variables.

Digital and analog computers compared. Among the merits of digital computers are higher computational accuracy and speed (up to several hundred thousand operations per second). Within a short time interval a digital computer can do the job that would take a team of human calculators many months to complete.

Digital computers are especially adapted to solving problems which involve iterative techniques or successive approximations. Digital computers are incorporated in design optimizing systems, optimizing control systems, and are used to represent large systems which cannot be simulated on analog computers[23-26]. Last but not least, digital computers handle statistical data on the activities of industrial organizations and management for the purpose of subsequent optimization studies. A classification of digital computers is shown in Fig. I-41.

In a first approximation, the cost of a digital computer may be taken to be a linear function of accuracy. With analog computers, the accuracy of

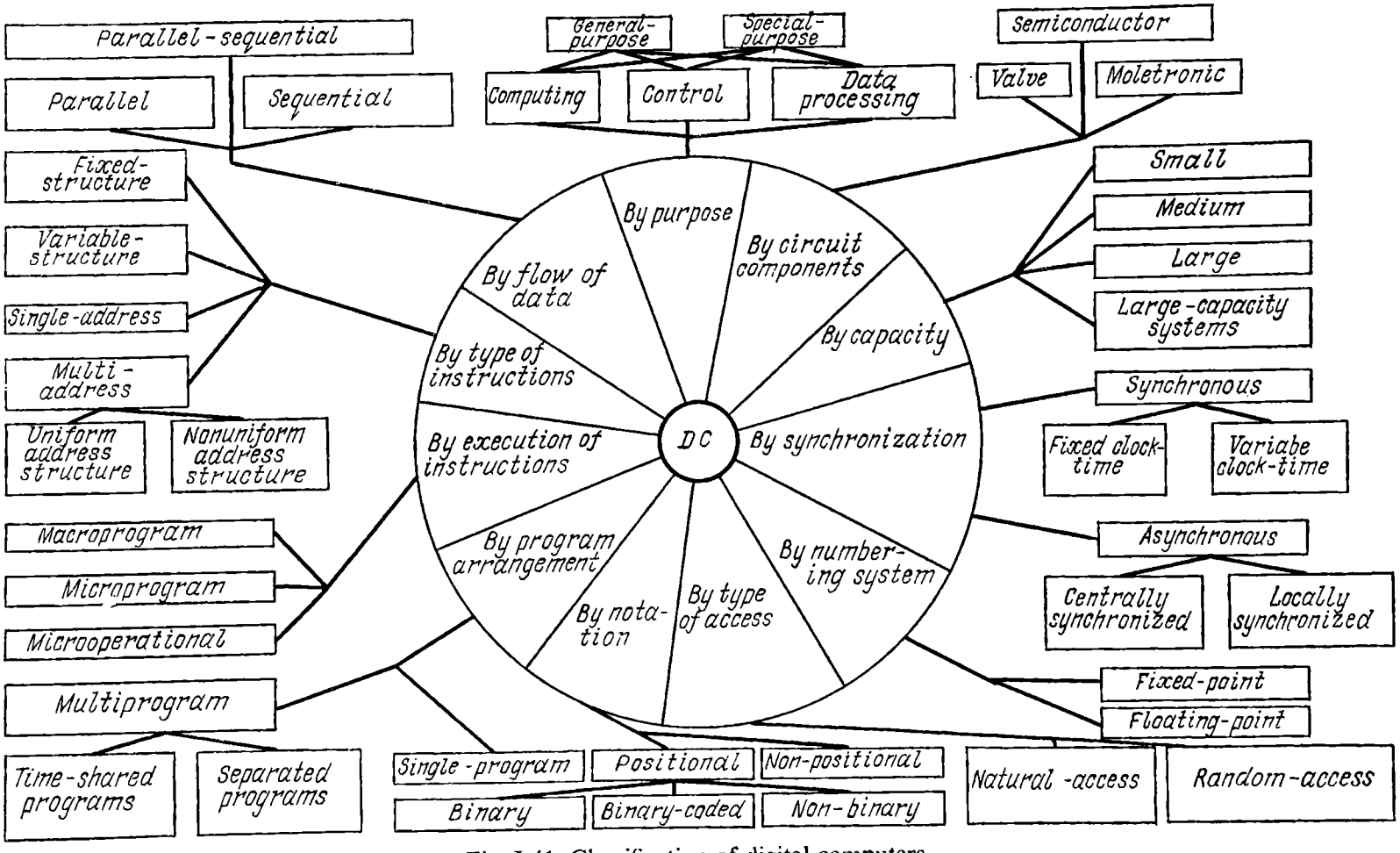


Fig. I-41. Classification of digital computers

solutions is decided by the accuracy with which the circuit elements are fabricated and their stability. With them, cost is no longer a linear function of accucary. In fact, it does not pay to build analog computers from precision circuit components made to tolerances better than 0.01%.

Apart from high accuracy, digital computers are flexible and more versatile. Yet, the choice of a particular type or class of computer depends on how it fits the problem(s) to be solved.

Three generations of computers. First-generation computers dating back to 1949-1950 used electronic valves throughout. They had no "prefabricated" software, and all programming was done by the user.

Second-generation computers, which appeared in 1950-1964, were built around discrete semiconductor devices. They had brought with them system programming, that is, program libraries, translators and compilers.

Third-generation computers which have been in operation since 1964 are based on integrated circuits. There have been changes in the computer system, too. Typically, a third-generation computer consists of a central processor, main storage, an appropriate number of input-output devices and, probably, other processors linked to the central processor by suitable channels and interfaces. Despite interfacing with the central processors, they can operate on their own, that is, on a decentralized basis.

Many of the operations in a computer are carried out all at a time. Some of the procedures which were executed by special subroutines in the past have now been wired into the computer structure. Among them are floating-point operations, double-precision computations, generation of some elementary functions, operations on variable-length words, etc. This also applies to some of testing and diagnostic functions.

Now that storage capacity has become practically unlimited and access methods have been refined to a great extent, the user is better off as regards programming, translation from different languages, data exchange, input and output operations. There is also a wide system of interrupts that enable the computers to operate on a time-sharing basis.

Further advances have been made in computer software. Work has been continued on problem-oriented languages for algorithms, circuit and system simulation and other applications, on machine-oriented symbolic languages like the Autocode, which are adapted to the capabilities of specific computers and models, and also on associated translators, compilers and a variety of auxiliary programs to facilitate the use of languages and translation. Programming languages have been taking on specialized functions, namely FORTRAN and ALGOL-60 for mathematical applications, COBOL for commercial problems, SIMSCRIPT, SOL and LOTIS for the simulation of logical functions, and PL/1 specifically worked out for the IBM/360 system.

Another important trend in the improvement of software has been the development of so-called *operating systems* and *service programs* which have greatly simplified problem programming and solving and relieved the programmer of the more "routine" tasks. Among them are above all de-

bugging programs, supervisor programs, archive file programs, and automatic option selection programs. These programs are combined into an operating system controlled by what is called a monitor or supervisor. These program systems also include diagnostic and testing programs which facilitate computer maintenance.

The biggest impetus to third-generation computers has been given by microelectronics, especially integrated circuits (ICs). According to the number of circuit elements interconnected within a single semiconductor chip, there are conventional integrated circuits (a few elements per chip), medium-scale integrated circuits (a few tens of elements) and large-scale integrated, or LSI, circuits (a few hundred or even thousand elements).

As regards the arithmetic unit, it has become possible to combine several units in the same physical device, namely a decimal unit, a binary unit, a floating- and a fixed-point unit, and also circuits to speed up computations with double precision. Because of the growing complexity in the functions performed, the arithmetic unit is infrequently referred to as a data processing unit or a data processor.

A wider variety of media have come to be used for computer memory. Among them are ferrite cores, thin magnetic films, LSI circuits, odd-shaped ferrites, magnetic discs and tapes. Memory (or storage) units as widely differ in capacity, access time and cost. The internal working memory mostly uses magnetic cores (hence the name "core memory" or "core storage"). Usually built as core arrays (for, say, 4096 words) such memory units have an access time of 0.5 μs and use cores about 0.5 mm in diameter. The total capacity of an internal working memory may be as high as 4 to 6 million bytes (one byte = eight bits). Thin-film storage units have already been developed to have a capacity warranting their use in computers (several thousand words). Although they are more expensive than core memory, it is believed that short access time will soon turn them into successful competitors for core memory. Memory units using LSI circuits have also reached the commercial status. With an access time as short as 10 to 25 ns, they can readily be interfaced with the remaining units of a computer in terms of both signals and design because they are made up of the same semiconductor devices as the logic circuits of the computer.

There is ground for believing that with a further decrease in reject percentage and improvements in manufacturing techniques, it will be possible to build large-scale integrated-circuit memory units of a super-large capacity and a low specific cost.

External memory uses magnetic drums (with a capacity of several million words and an access time of a few milliseconds), magnetic discs and cards (with a capacity of a few hundred million words and an access time of tens or hundreds of milliseconds), and magnetic tapes. Exchange of information between different memory units can be organized by special programs in the course of computations.

Third-generation computers are superior to their predecessors in terms of reliability, too. The contributing factors are the improved reliability of the

components, the extent of integration, and better instrumentation and programming techniques used.

A typical operating system functions as follows.

A package of jobs are fed into a computer, and the jobs are executed in the sequence selected by the operating system, usually in the multiprogramming mode. The user maintains contact with the computer on the shared-time basis (concurrent use of the computer by several users) and real-time basis. Each user has at its disposal an input-output terminal device, which may be a teleprinter or a CRT display, and the computer capabilities available are shared between all users. In real-time working, up to 1000 terminals may be used.

The user "converses" with the system, and his dialogue should be easy to grasp. The system, too, must be conversational, that is, it must be able to ask and answer questions, and do this with a minimum delay. The user should have a great number of auxiliary subroutines to help him with problem solving at any time.

The user does not, and ought not to, feel what the operating system does to maintain multiaccess operation.

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CHAPTER II

USE OF CYBERNETIC METHODS IN THE ANALYSIS OF CHEMICAL ENGINEERING PROCESSES

II-1. DEVELOPMENT OF A MATHEMATICAL MODEL FOR A CHEMICAL ENGINEERING PROCESS

Residence time distribution function. The structure of a mathematical model for any chemical-engineering process involving fluid flows is above all affected by the flow pattern(s) prevailing in the system and is reflected in the distribution of residence times of fluid elements in their passage through that system (which may be a reactor).

This distribution obeys statistical laws and can be ascertained from the form of a test signal passing through the system. A test signal may be simulated by injecting an amount of a tracer into the feed stream as a step input, or as an impulse, or a sinewave.

With a tracer injected instantaneously, its concentration is observed at the system outlet for a series of time intervals, and these data are plotted to give a C-diagram. This is the residence time distribution based on an impulse stimulus and can be described as

$$C = \int_0^\infty \tau C(\tau)\, d\tau \tag{II-1}$$

The residence time distribution function $C(\tau)$ gives the fraction of the indicator in the reactor exit stream that has spent a time less than τ within the reactor.

The average residence time $\bar{\tau}$ is given by

$$\bar{\tau} = \frac{\int_0^\infty \tau C(\tau)\, d\tau}{\int_0^\infty C(\tau)\, d\tau} \approx \frac{\sum \tau C}{\sum C} \tag{II-2}$$

The residence time distribution function may be written as

$$C(\tau) = \frac{1}{\tau}\frac{c}{c_0} = \frac{c}{\sum c\,\Delta\tau}\ \mathrm{s}^{-1} \tag{II-3}$$

where $\Delta\tau$ is the sampling interval.

The ratio

$$\theta = \tau/\bar{\tau} \tag{II-4}$$

is the dimensionless residence time.

Once the average residence time is known, the C-diagram may be described by an equation of the form

$$C = c/c_0 = \tau C(\tau) \tag{II-5}$$

where c_0 is the initial concentration at the system inlet.

The *spread*, or *variance*, of a given variable about its mean in the case of a sample from a continuous distribution for a finite number of equidistant points (equal sampling intervals) is given by

$$s_\tau^2 = \frac{\sum x_i^2 f(x_i)}{\sum f(x_i)} - \left[\frac{\sum x_i f(x_i)}{\sum f(x_i)}\right]^2 \tag{II-6}$$

For the variance in time units (s_τ^2), we have

$$\sum f(x_i) = \sum c_i \quad \sum x_i f(x_i) = \sum \tau_i c_i \quad \sum x_i^2 f(x_i) = \sum \tau_i^2 c_i \tag{II-7}$$

In units of dimensionless time, the variance is given by

$$s^2 = s_\tau^2/(\bar{\tau})^2 \tag{II-8}$$

For the C-distribution in dimensionless time, θ, we get

$$s^2 = \frac{\sum \theta^2 C}{\sum c} - 1 = \sum \theta^2 C\,\Delta\theta - 1 \tag{II-9}$$

A step change stimulus, as already noted, produces an exit response known as the F-diagram. The C- and F-diagrams, that is, the residence time distributions derived on the basis of an impulse and a step change stimulus, are related as follows

$$F = \int_0^\theta C\,d\theta \qquad C = dF/d\theta \tag{II-10}$$

The function $C(\tau)\,d\tau$ gives the fraction of material in the reactor exit stream which has spent a time between τ and $(\tau + d\tau)$ within the reactor. Multiplying it by the concentration of material, c_A, that has been in the fluid element of the age $\tau + d\tau$ gives the average concentration c_A of material leaving the reactor

$$\bar{c}_A = \int_{\tau=0}^{\tau=\infty} c_A C(\tau)\,d\tau \tag{II-11}$$

The determination of residence times for fluid elements from the above equations is based on the concept of statistical *moments* and the probability density function. The zeroth moment of a probability density function is unity. The first moment is the *expectation* or mean value of the ensemble which gives a measure of the location of the "centre" of the distribution. The second moment is the *variance* which gives a measure of the "spread" of the distribution. The third moment is a measure of the symmetry or *skewness* of the distribution with respect to the mean. The fourth moment characterizes the sharpness of the peak about the mode (*peakedness* or *kurtosis*).

Theoretically, the moments are calculated in the range from zero to infinity. For a continuous distribution they have the form:

$$\left.\begin{aligned} M_0 &= \int_0^\infty C(\tau)\, d\tau \\ M_1 &= \frac{\int_0^\infty \tau C(\tau)\, d\tau}{\int_0^\infty C(\tau)\, d\tau} \\ &\cdots\cdots\cdots\cdots \\ M_m &= \frac{\int_0^\infty \tau^m C(\tau)\, d\tau}{\int_0^\infty C(\tau)\, d\tau} \end{aligned}\right\} \qquad \text{(II-12)}$$

Since experimental distribution curves are usually approximated stepwise, it is assumed that the resultant distribution is discrete, and the expressions for the respective moments are as follows:

$$\left.\begin{aligned} M_0 &= \sum_{i=1}^{n} c_i \Delta\tau \\ M_1 &= \frac{\sum_{i=1}^{n} c_i \tau_i}{\sum_{i=1}^{n} c_i} \\ &\cdots\cdots\cdots\cdots \\ M_m &= \frac{\sum_{i=1}^{n} c_i \tau_i^m}{\sum_{i=1}^{n} c_i} \end{aligned}\right\} \qquad \text{(II-13)}$$

Unfortunately, Eqs. (II-13) lack in accuracy, especially if the experimental C-diagram has an extended tail.

A more accurate method for the estimation of distribution parameters is given below. It is based on the use of average ordinates of the C-diagram, with the limit of integration specified in advance. The procedure is as follows.

1. The moments for the experimental C-diagram are found by the trapezoid rule. Then for the zeroth moment we have

$$M_0^E = \int_0^a C\,d\tau \approx \sum_{i=1}^{n} c_{av,i}\Delta\tau \tag{II-14}$$

where $c_{av,i} = (c_{i+1}+c_i)/2$ is the average ordinate of the C-diagram in the interval $0-a$.

For any moment then:

$$M_j^E = \frac{\int_0^a \tau^j C\,d\tau}{\int_0^a C\,d\tau} = \frac{\int_0^a \left(\frac{c}{j+1}\right) d(\tau^{j+1})}{\int_0^a C\,d\tau}$$

$$\approx \frac{\sum_{i=1}^{n}\left(\frac{c_{av,i}}{j+1}\right)\Delta(\tau^{j+1})}{\sum_{i=1}^{n} c_{av,i}\Delta\tau} = \frac{\sum_{i=1}\left(\frac{c_{av,i}}{j+1}\right)(\tau_{i+1}^{j+1}-\tau_i^{j+1})}{\sum_{i=1}^{n} c_{av,i}\Delta\tau} \tag{II-15}$$

Using Eq. (II-15), the following expressions can be derived

$$M_1^E = \frac{\frac{1}{2}\sum_{i=1}^{n} c_{av,i}(\tau_{i+1}+\tau_i)}{\sum_{i=1}^{n} c_{av,i}} \tag{II-16}$$

$$M_2^E = \frac{\frac{1}{3}\sum_{i=1}^{n} c_{av,i}(\tau_{i+1}^2+\tau_{i+1}\tau_i+\tau_i^2)}{\sum_{i=1}^{n} c_{av,i}} \tag{II-17}$$

$$M_3^E = \frac{\frac{1}{4}\sum_{i=1}^{n} c_{av,i}(\tau_{i+1}+\tau_i)(\tau_{i+1}^2+\tau_i^2)}{\sum_{i=1}^{n} c_{av,i}} \tag{II-18}$$

etc.

With the interval chosen to be $\Delta\tau < 0.02\theta_{av}$, the estimation of distribution parameters from Eq. (II-15) yields results practically the same as the exact expressions, Eqs. (II-12).

2. Moments are then found for models with limits of integration from 0 to $\tau = a$, and not from zero to infinity, as is usually done, and a system

of equations of the form

$$\left.\begin{aligned} M_1^E &= M_1^M \\ M_2^E &= M_2^M \\ &\cdots\cdots\cdots \\ M_j^E &= M_j^M \\ &\cdots\cdots\cdots \\ M_m^E &= M_m^M \end{aligned}\right\} \qquad \text{(II-19)}$$

is solved, where the moment

$$M_j^M = \frac{\int_0^a \tau^j C\, d\tau}{\int_0^a C\, d\tau} \qquad \text{(II-20)}$$

is found from a model.

The choice of the breakpoint on the curve, $\tau = a$, depends on the conditions of measurement (the accuracy and sensitivity of measuring elements), because the experimental curve is used to estimate the correctness of the model itself. The number of equations in the system (II-19) depends on the number of model parameters. For some models, such as the cascade type or a tank with a stagnant zone (see p. 133), M_j^M can be expressed analytically. In cases where this cannot be done because of the complexity of analytical solutions for the equations of the model, M_j^M should be found by directly integrating the model equations.

Example II-1.[2] In deriving a mathematical model for a reactor, the following concentrations of tracer in the reactor exit stream have been observed after the imposition of a unit impulse stimulus (the delta function):

Time, min ...	0	5	10	15	20	25	30	35
Tracer concentration, g/m³ of stream ..	0	3	5	5	4	2	1	0

Plot a residence time distribution curve.

Solution. Find the distribution function $C(\tau)$ from Eq. (II-3). To begin with, determine the sum $\sum c\,\Delta\tau$ for a sampling interval $\Delta\tau = 5$ min:

$$\sum c\,\Delta\tau = (3+5+5+4+2+1)\times 5 = 100 \text{ g min/m}^3$$

The values of $C(\tau) = c/\sum c\,\Delta\tau$ at different times are as follows

τ, min	0	5	10	15	20	25	30
$C(\tau)$, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01

To find C, reduce the time to the dimensionless time θ and $C(\tau)$ to C. For this purpose, find the average residence time from Eq. (II-2) or (II-13):

$$\bar{\tau} = \frac{\sum \tau c}{\sum c} = \frac{(5\times 3)+(10\times 5)+ \ldots +(30\times 1)}{3+5+5+4+2+1} = \frac{300}{20} = 15 \text{ min}$$

On the basis of Eq. (II-4), the dimensionless time is

$$\theta = \tau/\bar{\tau} = \tau/15$$

Hence, by Eq. (II-5), we have

$$C = \tau C(\tau) = \frac{15c}{\sum c\,\Delta\tau}$$

On substituting the respective numerical values, we get

θ	0	$^1/_3$	$^2/_3$	1	$^4/_3$	$^5/_3$	2
C	0	0.45	0.75	0.75	0.60	0.3	0.15

From these data, plot the C-*vs*-θ distribution curve (Fig. II-1).

Frequency response. When a tracer material is injected into the reactor under study as a pure sine wave at a particular frequency, the response is likewise a pure sine wave of the same frequency and differs from the input stimulus only in magnitude and phase as dictated by the behaviour of the reactor. The resultant curve is called a *frequency response*.

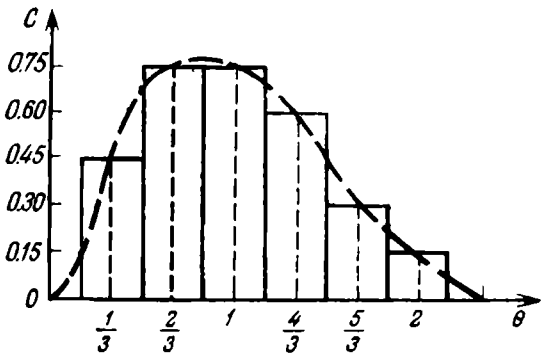


Fig. II-1. Probability distribution function (to Example II-1)

The frequency response of a reactor is usually interpreted in the frequency rather than the time domain through the use of the Laplace transform method. By this method, a function of a real time variable is transformed into a new function of a complex frequency variable, called a *direct Laplace transform*. The direct Laplace transform of a time function is defined as

$$F(p) = \int_0^\infty f(\tau)e^{-p\tau}\,d\tau \qquad \text{(II-21)}$$

or, in words, if a time function $f(\tau)$ describes the behaviour of a system in the time domain, it can be transformed into another function, $F(p)$, of a complex frequency variable, $p = j\omega$ (where $j = \sqrt{-1}$ and ω is the angular frequency). The function $f(\tau)$ is called the *original time function*, and $F(p)$ is its direct Laplace transform. The correspondence between the two is written as:

$$F(p) \doteqdot f(\tau)$$

or

$$F(p) = L[f(\tau)]$$

In the solution of integro-differential equations it is also required to recover the original time function from a given direct Laplace transform $F(p)$. This is called the *inverse Laplace transform* and is defined as

$$f(\tau) = \frac{1}{2\pi j} \int_{-j\infty}^{+j\infty} F(p) e^{p\tau} \, d\tau \tag{II-22}$$

The inverse Laplace transform operation is defined as

$$f(\tau) \doteqdot F(p)$$

or

$$f(\tau) = L^{-1}[F(p)] \tag{II-22a}$$

The direct and inverse Laplace transforms are referred to as a Laplace transform pair, and tables of these pairs are usually included in books on automatic control.

In solving differential equations by the Laplace transform method, the derivatives are replaced by the respective Laplace transforms according to the rules set forth below:

$$\left.\begin{aligned} \frac{df}{d\tau} &\doteqdot pF(p) - pf(0) \\ \frac{d^2f}{d\tau^2} &\doteqdot p^2F(p) - p^2f(0) - pf^1(0) \\ \frac{d^nf}{d\tau^n} &\doteqdot p^nF(p) - p^nf(0) - p^{n-1}f^1(0) - pf^{n-1}(0) \end{aligned}\right\} \tag{II-23}$$

In the special case where the initial conditions for the function $f(\tau)$ and the derivatives up to the $(n-1)$th order are zero, the above expressions are simplified as follows:

$$\left.\begin{aligned} \frac{df}{d\tau} &\doteqdot pF(p) \\ \frac{d^2f}{d\tau^2} &\doteqdot p^2F(p) \\ \frac{d^nf}{d\tau^n} &\doteqdot p^nF(p) \end{aligned}\right\} \tag{II-23a}$$

and the conversion of a derivative in the original equation into its Laplace transform reduces to multiplying $F(p)$ by p^n, where n is the order of the derivative.

Similarly, Laplace transforms can be derived for the integral terms in the source equations:

$$\left.\begin{aligned} \int_0^\tau f(\tau) \, d\tau &\doteqdot \frac{1}{p} F(p) \\ \int_0^\tau \cdots \int_0^\tau f(\tau) \, d\tau &\doteqdot \frac{1}{p^n} F(p) \end{aligned}\right\} \tag{II-24}$$

In the above equations, the operator p can be handled as any algebraic factor, that is, it can be placed outside brackets, cancelled, etc. As a result, the solution of integro-differential equations reduces to solving algebraic equations.

The ratio of the Laplace transform of an output time function to the Laplace transform of the respective input time function gives the *transfer function* of a system, defined as

$$W(p) = W(j\omega) = \frac{F(p)_{out}}{F(p)_{in}} = (a/A)e^{-j\varphi} \qquad \text{(II-25)}$$

where a/A is the ratio of the input and output signal amplitudes and φ is the phase lag of the output signal relative to the input stimulus.

From transfer functions developed for a wide range of frequencies, one can readily plot a frequency response diagram which can then be compared with that of the known frequency responses for standard reactor models. (The transfer functions of standard reactor models are summarized in Table II-1). The transfer function of a practical reactor can be evaluated by using a combination of several models.

Now we shall develop the transfer function for a continuous stirred tank reactor (often abbreviated C.S.T.R.) in which a first-order reaction takes place. The quantities involved will be designated as follows: the volumetric

Table II-1

Transfer Functions of Standard Idealized Models

Standard model	Transfer function	Remarks
Well-stirred	$\frac{1}{T_1p+1}$	$T_1 = V/V_q$, where V is the reactor volume, V_q is the fluid space velocity
Plug-flow	e^{-pT_d}	$T_d = L/w$ is the distance-velocity lag, where L is the reactor length, w is the linear velocity
m equal-size well-stirred tanks in a cascade	$\frac{1}{(T_1p+1)^m}$	—
m unequal-size well-stirred tanks in a cascade	$\frac{1}{(T_1p+1)(T_2p+1)\ldots(T_mp+1)}$	$T_1 = V_1/V_q$ ....
Plug-flow and well-stirred tanks in a cascade	$\frac{e^{-pT_d}}{T_1p+1}$	$T_m = V_m/V_q$

throughput or space velocity as V_q, the composition of the exit stream as c_{out}, the composition of the feed as c_{in}, the reaction rate constant as k, the reactor volume holdup as V, and the time as τ.

On the basis of the material balance, we have

$$V_q c_{in} - V_q c_{out} - kVc_{out} = V \frac{dc_{out}}{d\tau} \tag{II-26}$$

Taking the Laplace transform, we get

$$V_q c_{in}(p) - V_q c_{out}(p) - kVc_{out}(p) = Vc_{out}(p)p \tag{II-27}$$

where p is the Laplace operator.

Dividing the output by the input, we get

$$\frac{c_{out}(p)}{c_{in}(p)} = \frac{V_q/V}{(V_q/V+k+p)} \tag{II-28}$$

On putting $V/V_q = T$, then

$$\frac{c_{out}(p)}{c_{in}(p)} = \frac{1}{T(1/T+k+p)}$$

or

$$\frac{c_{out}(p)}{c_{in}(p)} = \frac{1}{Tp+Tk+1} \tag{II-29}$$

The above expression describes changes in the state of the system with time, that is, its transient response. Since c_{out}/c_{in} is usually measured under steady-state conditions under which p approaches zero, expression (II-29) may be reduced to the following form

$$\frac{c_{out}(0)}{c_{in}(0)} = \frac{1}{Tk+1} \tag{II-30}$$

From a comparison of Eq. (II-30) with the transfer function of a well-stirred tank reactor (see Table II-1), it is readily seen that the kinetic equation for a first-order reaction under steady-state conditions can be derived from the transfer function by replacing p with k. This offers a means for evaluating the kinetics of a process from its frequency response.

II-2. STANDARD MATHEMATICAL MODELS OF FLUID FLOWS IN REACTORS

On the basis of residence time distribution functions, all the multitude of mathematical models for the flows observed in various reactors can be reduced to a limited number of standard models which are presented below.

(A) PLUG-FLOW MODEL

In the plug-flow model, the reaction is assumed to proceed as the reactants in a plug progress along the reactor tube, but no interchange of material in the plug with material in either leading or following plugs takes place, and

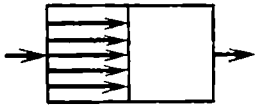
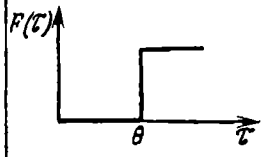
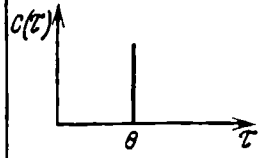
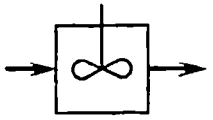
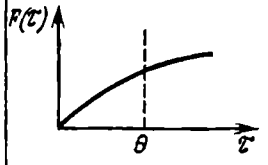
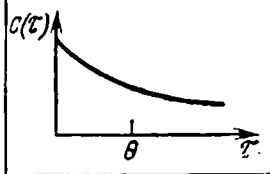
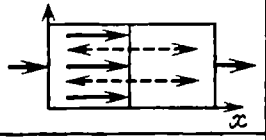
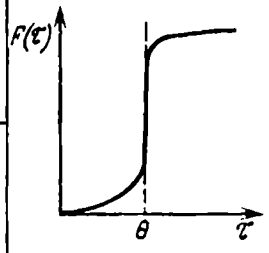
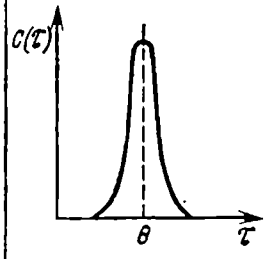
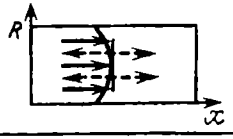
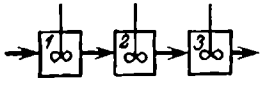
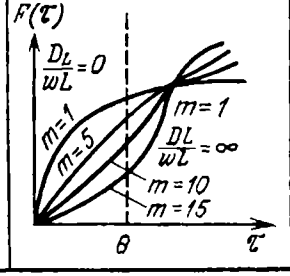
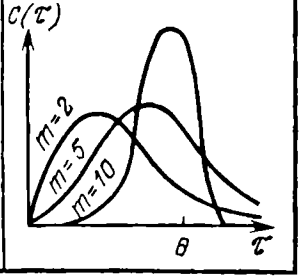
Standard models	Flow pattern	Mathematical model	Response to	
			step disturbance	impulse disturbance
1. Plug-flow		$\frac{\partial c}{\partial \tau} = -w\frac{\partial c}{\partial x}$		
2. Complete mixing (well-stirred)		$\frac{dc}{d\tau} = \frac{V_q}{V}(c_{in} - c_{out})$		
3. Dispersion: (a) single-parameter		$\frac{\partial c}{\partial \tau} = -w\frac{\partial c}{\partial x} + D_L\frac{\partial^2 c}{\partial x^2}$		
(b) two-parameter		$\frac{\partial c}{\partial \tau} = -w\frac{\partial c}{\partial x} + D_L\frac{\partial^2 c}{\partial x^2} + \frac{D_R}{R}\frac{\partial}{\partial R}\left(R\frac{\partial c}{\partial R}\right)$		
4. Cascade		$\frac{1}{m}\frac{dc_i}{d\tau} = \frac{V_q}{V}(c_{i-1} - c_i)$		

Fig. II-2. Typical flow patterns in chemical reactors

the reactants are uniformly distributed in the direction normal to the flow (Fig. II-2). The residence time is the same for all fluid elements and is equal to the ratio of the reactor volume to the volumetric throughput.

The mathematical model of the plug-flow reactor has the form

$$\partial c/\partial \tau = -w(\partial c/\partial x) \qquad \text{(II-31)}$$

where c is the concentration of the reactants (or energy), τ is the residence time, w is the linear flow velocity, and x is the coordinate (or position) along the tube.

The response curves for a step input stimulus, $F(\tau) = c/c_0$, and for an impulse stimulus, $C(\tau) = c/c_0$, are shown in Fig. II-2. From the form of the response curves it is seen that a plug-flow reactor is a pure-delay element (see p. 26). The response plots also show the dimensionless time, $\theta = \tau V_q/V$, where V_q is the volumetric throughput, V is the reactor volume holdup and τ is the time.

In a first approximation, the plug-flow model applies to processes occurring in tubular reactors with a tube length to diameter ratio of over 100.

(B) WELL-STIRRED TANK MODEL

In this model, the incoming reactants are assumed to be thoroughly mixed with the products very soon after entry to the vessel (see Fig. II-2). The inlet and exit concentrations are related as

$$dc/d\tau = \frac{V_q}{V}(c_{in} - c_{out}) \qquad \text{(II-32)}$$

The responses to a step and an impulse stimulus are shown in Fig. II-2. As is seen, a well-stirred tank model can be approximated by a simple-lag element.

The system response function has the form:

$$C(\tau)\, d\tau = \frac{V_q}{V} e^{-V_q \tau/V}\, d\tau = \frac{e^{-\tau/\bar{\tau}}}{\tau}\, d\tau \qquad \text{(II-33)}$$

where $\bar{\tau}$ is the system average residence time.

The well-stirred tank model applies to processes taking place in a cylindrical vessel having a spherical bottom and reflecting walls, with the contents intensively stirred.

(C) DISPERSION MODEL

There may be one-parameter and two-parameter dispersion models (see Fig. II-2).

One-parameter dispersion model. At the basis of this model is the plug flow of a fluid through a tubular reactor with some degree of backmixing obeying the formal law of diffusion, superimposed on the plug flow. The parameter of the model is the turbulent diffusion coefficient or the longitudinal dispersion coefficient, D_L. In developing a one-parameter dispersion

model, the following assumptions are usually made: the change in concentration is a continuous function of the distance (position) along the tube, the concentration is constant in a given cross-section, the space velocity of the stream and the longitudinal dispersion coefficient remain unchanged along the length and over the cross-section of the stream.

With these assumptions, the model will be described by the following equation:

$$\partial c/\partial \tau = -w(\partial c/\partial x) + D_L(\partial^2 c/\partial x^2) \qquad \text{(II-34)}$$

Equation (II-34) differs from Eq. (II-31) by an additional term, $D_L\,\partial^2 c/\partial x^2$, allowing for the turbulent diffusion or dispersion (see below). The quantity D_L is found by experiment.

Two-parameter dispersion model. This model takes into account both longitudinal and radial dispersion. Hence, there are a longitudinal dispersion coefficient, D_L, and a radial dispersion coefficient, D_R. It is assumed that neither D_L nor D_R changes along the length and over the cross-section of the reactor, and the flow velocity remains constant.

Assuming a tubular reactor of radius R in which the feed stream flows at a velocity remaining constant with length and over cross-section, a two-parameter dispersion model can be described by an equation of the form

$$\partial c/\partial \tau = -w(\partial c/\partial x) + D_L(\partial^2 c/\partial x^2) + (D_R/R)(\partial/\partial R)(R\,\partial c/\partial R) \qquad \text{(II-35)}$$

In experimental determinations, the longitudinal and radial dispersion coefficients, D_L and D_R, are usually represented as dimensionless groups known as Péclét numbers $\mathrm{Pe} = wL/D_L$ or $\mathrm{Pe}_R = wL/D_R$, where L is the characteristic length of the system. Then the equation of a dispersion model reduces to a dimensionless form by introducing a dimensionless concentration, $c/c_0 = C$, a dimensionless length $l/L = z$, and a dimensionless time, $\tau = L/w = V/V_q$, where V is the system volume holdup and V_q is the space velocity of the flow.

Recalling that the space flow velocity is assumed to be constant, Eq. (II-34) reduces to the form

$$-\frac{dC}{dz} + \frac{D_L}{wL}\frac{d^2C}{dz^2} = 0 \qquad \text{(II-36)}$$

If $D_L/wL = 0$ ($\mathrm{Pe} = \infty$), the dispersion model becomes a plug-flow model; if $D_L/wL = \infty$ ($\mathrm{Pe} = 0$), the dispersion model becomes a well-stirred tank model.

The responses of a dispersion model to a step and an impulse stimulus are shown in Fig. II-2.

When the deviation from plug flow conditions is small, the exit distribution (the C-diagram) is very well approximated by the normal error or Gaussian distribution for which the variance is

$$s^2 = 2\frac{D_L}{wL} \qquad \text{(II-37)}$$

(D) CASCADED REACTOR MODEL

The basis of the model is a cascade of well-stirred single-tank reactors with no mixing between the tanks (see Fig. II-2). The model parameter is the number m of well-stirred single-tank reactors.

Mathematically, a cascaded reactor system is described by m first-order linear differential equations of the form

$$\frac{1}{m} \cdot \frac{dc}{d\tau} = (V_q/V)(c_{i-1} - c_i) \tag{II-38}$$

where $i = 1, 2, \ldots, m$.

The distribution given by the C-curve is related to the number m of stirred tanks in a cascade by

$$C = c/c_0 = \frac{m\theta^{m-1}}{(m-1)!} e^{-m\theta} \tag{II-39}$$

where $\theta = \tau/(V/V_q)$, for which the variance s^2 is

$$s^2 = 1/m = 2D_L/wL - 2(D_L/wL)^2 (1 - e^{-wL/D_L}) \tag{II-40}$$

or, with an accuracy sufficient for all practical purposes at $m > 10$

$$s^2 = 1/m = 2D_L/wL \tag{II-40a}$$

At $m = 1$, the cascade reduces to a well-stirred single-tank reactor, while at $m = \infty$, it turns to a plug-flow model.

The responses of a cascaded reactor system to a step and an impulse stimulus appear in Fig. II-2.

In the case of a cascaded reactor system, the first two moments of the distribution, as found experimentally, are given by

$$M_1^M = \frac{m}{b}\left\{1 - e^{-bx}\left[\frac{(bx)^m}{m!} + \frac{(bx)^{m-1}}{(m+1)!} + \ldots + \frac{(bx)^2}{2!} + bx + 1\right]\right\}$$

$$M_2^M = \frac{(m+1)m}{b^2}\left\{1 - e^{-bx}\left[\frac{(bx)^{m+1}}{(m+1)!} + \frac{(bx)^m}{m!} + \ldots + \frac{(bx)^2}{2!} + bx + 1\right]\right\}$$

where

$$b = m\varepsilon \qquad \varepsilon = \frac{M_1^E}{V/V_q} \qquad x = \frac{a}{M_1^E}$$

$$M_1^M = \left(\frac{M_1^E}{M_1^E}\right) = 1 \qquad M_2^M = \frac{M_2^E}{(M_1^E)^2}$$

Besides M_1^E is the first moment of the distribution found experimentally, M_2^E is the second moment likewise found experimentally and a is the time at the end of the experiment.

The cascaded model applies to a cascade of well-stirred reactors, absorption and extraction columns under certain flow-pattern conditions and, to a first approximation, to fluidized-bed reactors.

The transfer functions of standard idealized models are presented in Table II-1.

Hybrid Models of Continuous Flow Reactors

Model	Parameter	Characteristics	Applications
		Hybrid well-stirred model	
1. Well-stirred with a stagnant region	m	(a) $V_1 = V_4 = V$; $V_2 = V_3 = 0$; $b_1 = b_2 = b_3 = d_1 = 0$ (b) $m + d_2 = 1$	Low-rate mixing in cylindrical or rectangular vessels
2. Plug-flow with a stagnant region	b	(a) $V_1 = V_3 = V$; $V_2 = V_4 = 0$; $b_2 = b_3 = m = d_2 = 0$; $b_1 = b$ (b) $b + d_1 = 1$	Stationary bed; extraction columns
3. Well-stirred with short-circuiting (see p. 307)	V_3 or V_4	(a) $V_1 = V$; $V_2 = 0$; $b_1 = b_2 = b_3 = 0$; $d_1 = d_2 = 0$ (b) $m = 1$ (c) $V_3 + V_4 = V$	Mixing with high feed rates and a short distance between inlet and outlet
4. Plug-flow with short-circuiting (see p. 307)	V_1 or V_2	(a) $V_3 = V$; $V_4 = 0$; $b = 0$; $b_2 = b_3 = 0$; $d_1 = d_2 = 0$ (b) $b_1 = 1$ (c) $V_1 + V_2 = V$	Packed-bed reactors; extraction columns
5. Parallel plug-flow regions	b_1 or b_2	(a) $V_3 = V$; $V_4 = 0$; $m = 0$; $b_3 = 0$; $d_1 = d_2 = 0$ (b) $b_1 + b_2 = 1$; $V_1 + V_2 = V$	Fluidized bed; packed-bed reactors; extraction columns
6. Well-stirred and plug-flow regions in cascade	m or b	(a) $V_1 = V_4 = V$; $V_2 = V_3 = 0$; $b_1 = b$; $b_2 = b_3 = d_1 = d_2 = 0$ (b) $m + b = 1$ (c) well stirred: $b = 0$ plug flow: $m = 0$	Stirred reactors with feed through lid; stationary layers; streams in tubes; packed-bed reactors; extraction columns
7. Well-stirred and plug-flow regions in parallel	m or b V_3 or V_4	(a) $V_1 = V$, $V_2 = 0$ $b_1 = b_2 = 0$; $b_3 = b$, $d_1 = d_2 = 0$ (b) $b + m = 1$ (c) $V_3 + V_4 = 1$	Stirred reactors with feed through bottom and outlet through lid, well stirred at agitator blades; fluidized bed

Table II-2 (continued)

Model	Parameter	Characteritics	Applications
		Hybrid well-stirred model	
8. Well-stirred with short-circuiting (see p. 307) and stagnation region	m, V_3 or V_4	(a) $V_1 = V$, $V_2 = 0$, $b_1 = b_2 = b_3 = 0$ $d_2 = 0$ (b) $V_3 + V_4 = V$, $m + d_2 = 1$	Stirred reactors; inlet and outlet through lid, with agitator well clear of bottom
		Hybrid model with a bypass	
Various combinations of regions	ε, η	(a) with factors corrected for each particular combination; (b) well stirred: $\eta = 1$, $\theta = 0$; plug flow: $\varepsilon/\tau_n = 1$, $\eta = 0$	Stirred reactors; flows in tubes; fluidized bed; absorption columns
		Model with recycling	
1. Recycling through two parallel plug flows	N, V_1 or V_2 b_1 or b_2	(a) $V + V_2 = V_1$; (b) $b_1 + b_2 = 1$	Stirred reactors with internal recycling
2. Recycling over three different closed circuits	N, r/V	(a) Well stirred with some residence in each circuit; (b) same transfer function for all circuits; (c) well stirred: $r/V = \infty$	Stirred reactors with high-rate internal recycling
3. Recycling above plug flow region	N, V_1 or V_2	(a) $b_1 = 1$, $b_2 = 0$ (b) $V + V_2 = V_1$ (c) $V_2 \ll V$	Same
		Cascaded model	
n well-stirred single-tank reactors in a cascade	n	(a) same size and perfect stirring in each tank (b) plug flow: $n = \infty$ (c) well-stirred $n = 1$	Stirred reactors; fluidized bed; absorption columns; extraction columns; rotating-plate columns; gas-liquid contact reactors; stationary layers

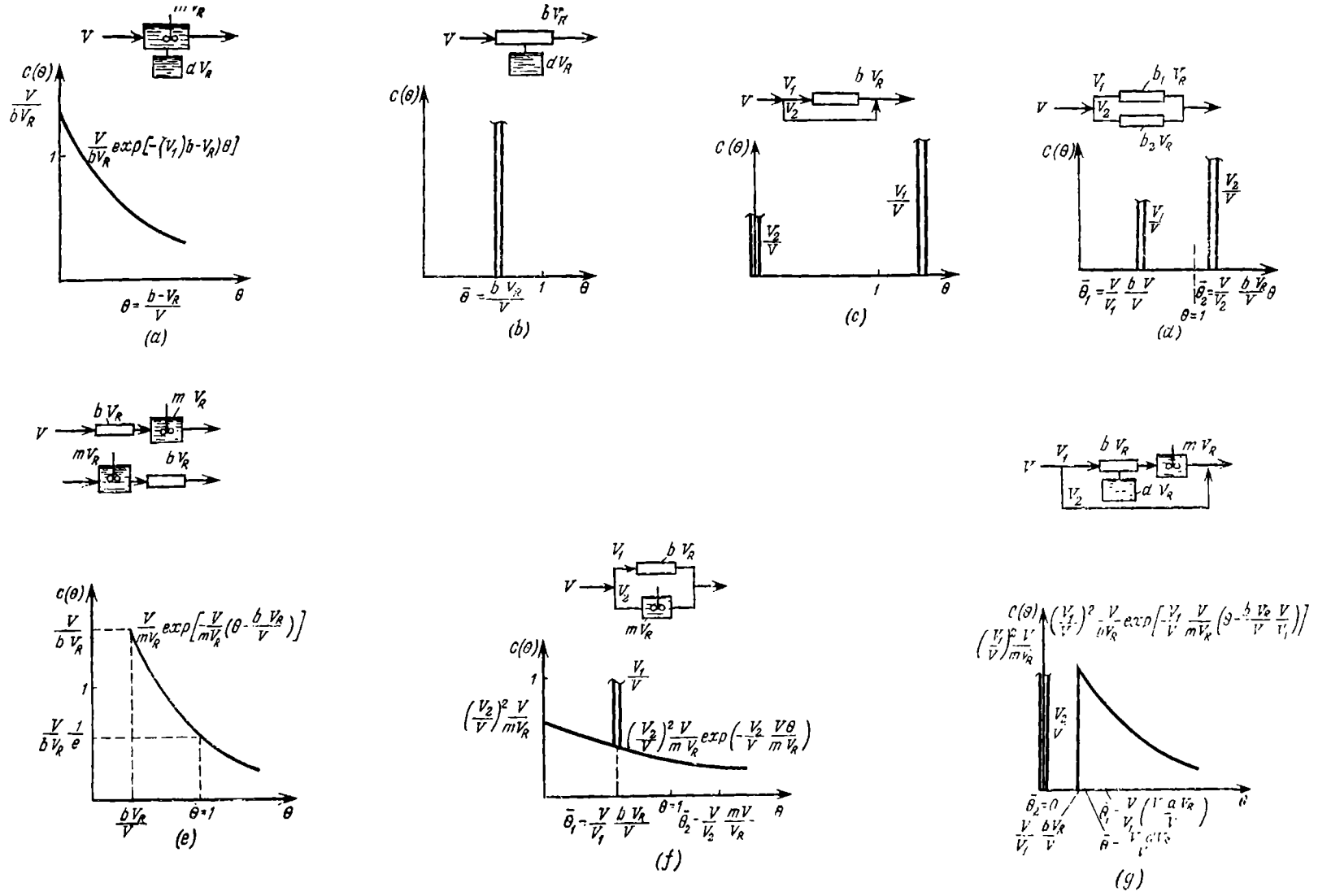


Fig. II-3. Impulse responses of simple hybrid reactor models

v, v_1, v_2 — volumetric throughput; V_R — reactor hold-up; b — plug-flow fraction; m — mixed zone fraction; d — stagnant-zone fraction

(E) HYBRID MODELS

Not all real processes can be described by the above models. This, above all, applies to processes incorporating bypasses and recycles, and also to processes with stagnant zones. This is where resort has to be made to hybrid models.

In deriving a hybrid model, it is assumed that the reactor consists of several zones or regions connected in series or parallel, as the case may be, with different flow patterns, namely a plug-flow zone, a perfect mixing zone, a longitudinal-dispersion zone, or a stagnant zone. In addition, as already

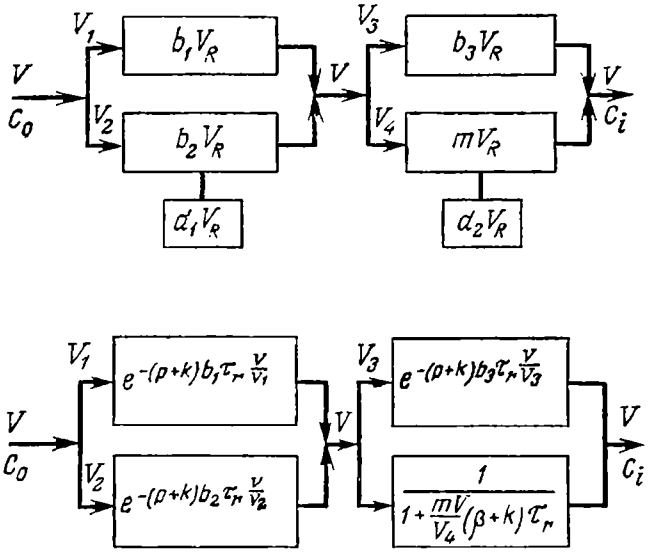


Fig. II-4. Model and block-diagram of a hybrid well-mixed reactor

noted, there may be local flows, such as bypasses, recycles, short-circuiting, etc.

Which of the above flow patterns is present is found from the responses of the system to various test stimuli. It may be noted that by increasing the number of zones it is possible to describe any process, however complex, but mathematical modelling will be complicated in proportion.

The responses of a few hybrid models to an impulse stimulus, along with the reactor layout, are shown in Fig. II-3.[2]

We shall examine five of the wide variety of continuous flow reactors presented in Table II-2 in which first-order reactions take place.[3] In calculating any reactor, it will be assumed that no reaction is under way, so that the reaction rate constant is $k = 0$. The discussion will also include the respective transfer functions, step, impulse and frequency responses.

In analysing a real reactor under specific conditions, it is always possible to approximate it with one of the models presented in Table II-2.

Hybrid well-stirred tank model (Fig. II-4). There are two circuits comprising three plug-flow zones (*b*), a well-stirred zone (*m*) and two stagnant

zones (*d*). The transfer function of the model has the form:

$$W(p) = \sum_1^2 \left[\frac{\frac{V_1 V_3}{V^2} e^{-\frac{V}{V_1} b_1 (p+k)\tau_r}}{1 + \frac{m V \tau_r}{V_4}(p+k)} + \frac{V_1 V_3}{V^2} e^{-\frac{V}{V_1} b_1 (p+k)\tau_r - \frac{V}{V_3} b_3 (p+k)\tau_r} \right] \quad \text{(II-41)}$$

The impulse response is given by

$$C = \frac{c_i}{c_0}(\theta) = \sum_1^2 \frac{V_{i1} V_3}{V^2} e^{-\frac{V}{V_{i1}} b_1 k\tau_r - \frac{V}{V_3} b_3 k\tau_r} \delta\left(\theta - \frac{V}{V_1} b_1 - \frac{V}{V_3} b_3\right)$$
$$+ \frac{V_{1i} V_4^2}{m V_3} e^{-\frac{V}{V_{i1}} b_i k\tau_r - \left(k\tau_r + \frac{V_4}{mV}\right)\left(\theta - \frac{V}{V_i} b_i\right)} \nu\left(\theta - \frac{V}{V_1} b_1\right) \quad \text{(II-42)}$$

The step response function is:

$$F = \frac{c_i}{c_0}(\theta) = \sum_1^2 \left\{ \frac{V_{i1} V_4^2}{m V_3} \cdot \frac{e^{-\frac{V}{V_{i1}} b_1 k\tau_r}}{k\tau_r + \frac{V_4}{mV}} \left[1 - e^{-\left(k\tau_r + \frac{V_4}{mV}\right)\left(\tau - \frac{V}{V_{i1}} b_{i1}\right)} \right] \nu\left(\tau - \frac{V}{V_{i1}} b_{i1}\right) \right.$$
$$\left. + \frac{V_{i1} V_3}{V_2} e^{-\frac{V}{V_{i1}} b_{i1} k\tau_r - \frac{V}{V_3} b_3 k\tau_r} \nu\left(\theta - \frac{V}{V_{i1}} b_{i1} - \frac{V}{V_3} b_3\right) \right\} \quad \text{(II-43)}$$

where V, V_1 through V_4 are the space velocities, b_1 through b_3 are fractions of plug-flow zones, m is the fraction of the well-stirred zone, $\delta(\tau)$ is the unit impulse response, $\nu(\tau)$ is the unit step response, p is the Laplace operator, k is the reaction rate constant, $\tilde{\tau}_r = V_R/V$ is the mean residence time (V_R is the reactor volume), and $\theta = \tau/\tau_r$ is the dimensionless time.

Hybrid model with a bypass (Fig. II-5). There are a plug-flow zone, a well-stirred zone, a stagnant zone, a time-lag zone, and a bypass. The transfer function of the model has the form:

$$W(p) = \frac{e^{-p\varepsilon - k(\varepsilon - \tau_L)}}{\frac{\tau_r}{\gamma_i}(p+k) + 1} \quad \text{(II-44)}$$

The impulse response is given by

$$C = \frac{c_i}{c_0}(\theta) = \gamma_i e^{-k(\varepsilon - \tau_L) - (k\tau_r + \gamma_i)\left(\theta - \frac{\varepsilon}{\tau_r}\right)} \delta\left(\theta - \frac{\varepsilon}{\tau_r}\right) \quad \text{(II-45)}$$

and the step input response is

$$F = \frac{c_i}{c_0}(\theta) = \frac{e^{-k(\varepsilon - \tau_L)}}{k\tau_r + \gamma_i} \left[1 - e^{-(k\tau_r + \gamma_i)\left(\theta - \frac{\varepsilon}{\tau_r}\right)} \right] \nu\left(\theta - \frac{\varepsilon}{\tau_r}\right) \quad \text{(II-46)}$$

where ε is the phase shift of the system (in units of τ); γ_i is the mixing efficiency ($\gamma_i = 1$ in the case of perfect mixing, and $\gamma_i = 0$ in the case of perfect plug flow), τ_L is the time lag.

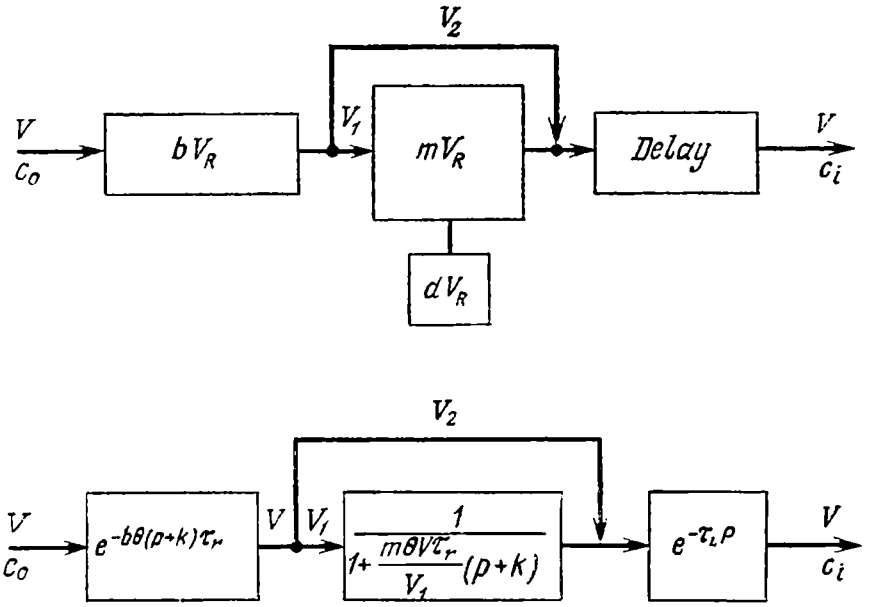


Fig. II-5. Model and block-diagram of a hybrid reactor with a bypass

Hybrid model with recycling and plug-flow zones (Fig. II-6).

The transfer function is:

$$W(p) = \frac{\frac{V}{V_1} e^{-(p+k)\tau_r \frac{b_1 V}{V_1}}}{1+\frac{V_2}{V_1} e^{-(p+k)\tau_r \left(\frac{b_1 V}{V_1}+\frac{b_2 V}{V_2}\right)}} \tag{II-47}$$

The impulse response is:

$$C = \frac{c_i}{c_0}(\theta) = \frac{V}{V_1} e^{-k\tau_r \frac{b_1 V}{V_1}} \sum_{N=1}^{N} \left\{ \left[\frac{V_2}{V_1} e^{-k\tau_r \left(\frac{b_1 V}{V_1}+\frac{b_2 V}{V_2}\right)} \right]^{N-1} \times \delta\left(\theta - \frac{N b_1 V}{V_1} + \frac{(N-1) b_2 V}{V_2}\right) \right\} \tag{II-48}$$

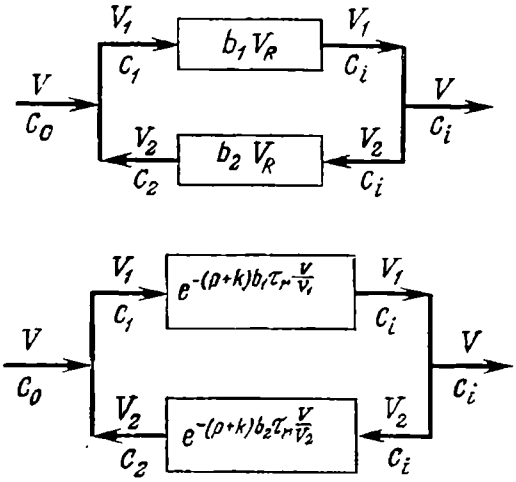


Fig. II-6. Model and block-diagram of a hybrid reactor with recycle and plug-flow zones

and the step input response is

$$F = \frac{c_i}{c_0}(\theta) = \frac{V}{V_1} e^{-k\tau_r \frac{b_1 V}{V_1}} \sum_{N=1}^{N} \left\{ \left[\frac{V_2}{V_1} e^{-k\tau_r \left(\frac{b_1 V}{V_1}+\frac{b_2 V}{V_2}\right)} \right]^{N-1} \times \nu\left(\theta - \frac{N b_1 V}{V_1} - \frac{(N-1) b_2 V}{V_2}\right) \right\} \tag{II-49}$$

where N is the number of recycles.

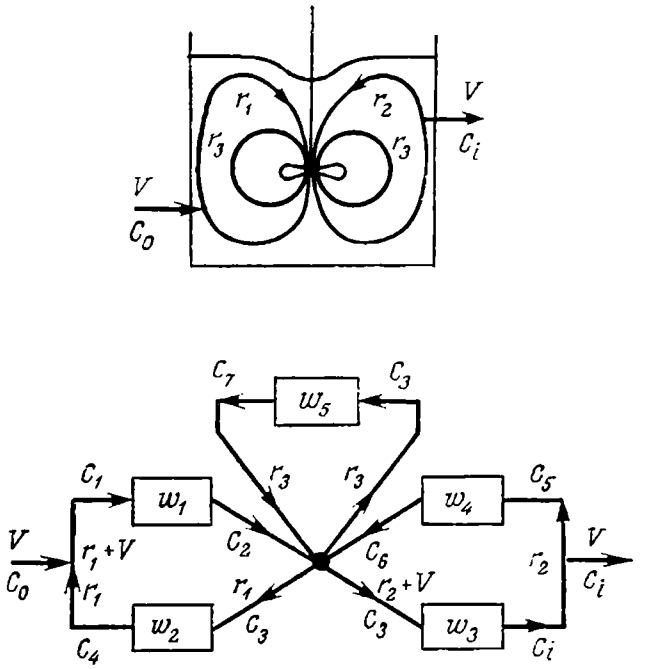


Fig. II-7. Model and block-diagram of a hybrid reactor with three recycles

Hybrid model with recycling over three closed circuits (Fig. II-7). The transfer function of the model is:

$$W(p) = \frac{\frac{V}{V+r}\left[\frac{N(V+r)}{V\tau_r}\right]^N}{\left[\frac{N(V+r)}{V\tau_r}+p+k\right]^N - a^N} \tag{II-50}$$

Its impulse response is

$$C = \frac{c_i}{c_0}(\theta) = \left(\frac{V+r}{r}\right)^{\frac{N-1}{N}} e^{-k_N\theta} \sum_{i=0}^{N-1} \left\{ e^{a\tau_r\theta\cos\frac{2\pi i}{N}} \cos\left(a\tau_r\theta \sin\frac{2\pi i}{N} + \frac{2\pi i}{N}\right)\right\} \tag{II-51}$$

and the step input response is

$$F = \frac{c_i}{c_0}(\theta) = \frac{\frac{V}{r}(a\tau_r)^N}{k_N^N - (a\tau_r)^N} + \left(\frac{V+r}{r}\right)^{\frac{N-1}{N}} e^{-k_N} \times \sum_{i=0}^{N-1} \frac{\left[a\tau_r \cos\left(a\tau_r\theta \sin\frac{2\pi i}{N}\right) - k_N \cos a_1\right]}{a_2 e^{-a\tau_r \cos\frac{2\pi i}{N}}} \tag{II-52}$$

where $r = r_1+r_2+r_3$ is the recycling space velocity and N is the number of recycles.

Also:

$$a = \frac{N(V-r)}{V\tau_r}\left(\frac{r}{V+r}\right)^{1/N} \qquad a_1 = \frac{2\pi i}{N} + a\tau_r\theta \sin\frac{2\pi i}{N}$$

$$a_2 = \left(a\tau_r \cos\frac{2\pi i}{N} - k_N\right)^2 + \left(a\tau_r \sin\frac{2\pi i}{N}\right)^2$$

$$k_N = k\tau_r + \frac{N(V+r)}{V}$$

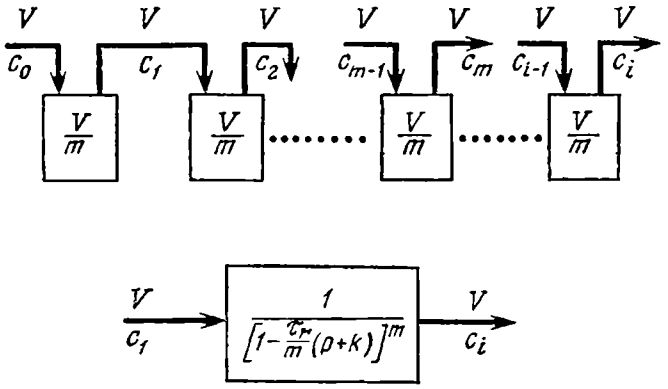


Fig. II-8. Model and block-diagram of a cascade reactor system

Cascade of equal-sized well-stirred tanks (Fig. II-8). The transfer function is given by

$$W(p) = \frac{1}{\left[1+\frac{\tau_r}{m}(p+k)\right]^m} \tag{II-53}$$

while its impulse and step input responses respectively are:

$$C = \frac{c_i}{c_0}(\theta) = \frac{m(m\theta)^{m-1}}{(m-1)!}e^{-m\theta\left(1+\frac{k\tau_r}{m}\right)} \tag{II-54}$$

and

$$F = \frac{c_i}{c_0}(\theta) = \left[\frac{1}{\left(1+\frac{k\tau_r}{m}\right)^m} - \frac{e^{-m\theta\left(1+\frac{k\tau_r}{m}\right)}}{\left(1+\frac{k\tau_r}{m}\right)^m}\right]\sum_{i=0}^{m-1}\left[\frac{1}{i!}(m\theta)^i\left(1+\frac{k\tau_r}{m}\right)^i\right] \tag{II-55}$$

where m is the number of well-stirred tanks.

The above equations are developed in the manner which will be clear from the following example where the model has two plug-flow regions and a recycle (see Fig. II-6), and its behaviour is interpreted from its response to an impulse stimulus.

The material balance about the first region may be written as

$$\partial c/\partial\tau = -\frac{V_1}{b_1}\cdot\frac{\partial c}{\partial V_R} - kc \tag{II-56}$$

Taking the Laplace transform of Eq. (II-56) under initial and boundary conditions such that

$$\begin{aligned} c &= 0 \quad \text{at} \quad \tau = 0 \\ c &= c_1 \quad \text{at} \quad V_R = 0 \end{aligned} \tag{II-57}$$

we get

$$\frac{c_i(p)}{c_1(p)} = e^{-(k+p)\frac{b_1 V_R}{V_1}} \tag{II-58}$$

Since $\tau_r = V_R/V$, Eq. (II-58) takes the form

$$\frac{c_i(p)}{c_1(p)} = e^{-(p+k)b_1\tau_r(V/V_1)} \tag{II-59}$$

Similarly, for the second region

$$\frac{c_2(p)}{c_i(p)} = e^{-(p+k)b_2\tau_r(V/V_2)} \tag{II-60}$$

Equations (II-59) and (II-60) describe two blocks in the diagram of Fig. II-6. The overall transfer function of the entire system is found from the material balance at the exit from the system (see Fig. II-6).

In the Laplace operator form, the impulse change in the inlet concentration is related to the subsequent change in outlet concentration as follows

$$c_i(p) = c_0 W(p) \tag{II-61}$$

Noting Eq. (II-23), the impulse response of the system may be described as

$$\frac{c_i(\tau)}{c_0} = L^{-1}[W(p)] = \frac{V}{V_1} e^{-k\tau_r b_1 \frac{V}{V_1}} L^{-1}\left\{\frac{e^{-p\tau_r b_1 \frac{V}{V_1}}}{1 - \frac{V_2}{V_1}\exp\left[-(p+k)V\tau_r\left(\frac{b_1}{V_1} - \frac{b_2}{V_2}\right)\right]}\right\} \tag{II-62}$$

Applying the expansion into a series to the last term and taking the inverse Laplace transform, we obtain

$$\begin{aligned} \frac{c_i}{c_0}(\tau) = \frac{V}{V_1} e^{-k\tau_r b_1 V/V_1} \sum_{N=1}^{N} \left[\frac{V_2}{V_1} e^{-k\tau_r\left(\frac{b_1 V}{V} + \frac{b_2 V}{V_2}\right)}\right]^{N-1} \\ \times \delta\left(\tau - \frac{N b_1 V \tau_r}{V_1} + \frac{(N-1) b_2 V \tau_r}{V_2}\right) \end{aligned} \tag{II-63}$$

Putting $\theta = \tau/\tau_r$, we recover the impulse response expressed by Eq. (II-48).

To find the step response by the above technique, we use the relation

$$\frac{c_i(\tau)}{c_0} = L^{-1}\frac{W(p)}{p} \tag{II-64}$$

II-3. BASIC STEPS IN MATHEMATICAL PROCESS MODELING

Model selection and building. In each particular case, a mathematical model is built according to the objectives of the process and process study, the accuracy desired, and the confidence in the source data used. This is usually a sequential process, because as an initial formulation is completed and research proceeds, the model is subjected to almost continuous and progressive reformulation.

Model building is the most delicate and critical part of mathematical modeling. What is important is not only and not so much a knowledge of mathematics as deep insight into the events described. As regards models for chemical-engineering processes, the chemical-reaction engineer can gain a sure foothold through the mastery of cybernetic methods.

In building any model, a formalized statement is above all sought for the prototype system. Most often, this is done by the block-diagram method (see p. 17). With this method, one starts with an analysis of each "elemental" process taking place in the prototype system. This analysis is conducted under conditions closely approaching those under which the prototype system is operated.

To begin with, the flow pattern of an elemental process is investigated to supply a foundation for mathematical formalism. Then comes the turn of chemical reaction kinetics, mass and heat transfer which are evaluated in the light of the flow patterns already elucidated. Now, a mathematical formalism is set up for each process, and these individual formalisms (usually in the form of a transfer function) are combined as blocks to build an overall mathematical description of the prototype system. A major advantage of the block-diagram method is that it can be used while the prototype system is in its drafting-board stage and the final physical embodiment is unknown yet.

The following groups of equations may be singled out of the *mathematical formalism* based on the physical behaviour of the prototype system:

1. *Mass and energy balances*, developed with allowance for existing flow patterns. These equations describe the distributions of temperature, composition and associated properties (such as density, viscosity, specific heat, etc.) in the flows.

2. "*Elemental*" *process equations* for local fluid elements. These equations cover mass and heat transfer, chemical reactions, etc.

3. *Theoretical, semi-empirical and empirical relations* between the various process variables, such as the dependence of the mass transfer coefficient on phase flow velocity, the dependence of the specific heat of a solution on its composition, etc.

4. *Limitations on process variables.* In building a model for some processes, one has to reckon with the limitations objectively imposed on the range of change for some variables.

When knowledge of the prototype system is scanty or lacking altogether,

so that even an approximate form of the governing equations is unknown, the mathematical description may be a collection of empirical relations derived through statistical observations of an operating system. Such models are statistical; they usually take the form of correlation or regression relations between the input and output variables of the system. Such relations can be derived only if there is an operating system on which a certain amount of experimentation can be carried out. A major drawback of statistical models is that the process variables can only be changed within relatively narrow limits; an attempt to extend the range of changes might lead to fairly complicated relations. Naturally, such models do not display the physical properties of the prototype system, and this handicaps a proper evaluation of the results.

In contrast to statistical models, a more accurate presentation of the prototype system is given by mathematical models built on the basis of functional relationships, even though the model parameters may be insufficient quantitatively. This is why these models may be used to investigate the general properties of prototype systems belonging to a particular class.

In *selecting a model*, the following points should be borne in mind:

— a model should fully represent the flows of substance and energy in terms of a sufficiently simple mathematical symbolism;

– model parameters should be amenable to determination by experiment or in any other way;

— with heterogeneous systems, a separate model should be selected for each phase; the models for both phases may be identical or different (for example, in the case of a plate-type mass-exchange reactor, a plug-flow model for the vapour or gas phase and a well-stirred model for the liquid phase);

— with homogeneous systems, a lumped-parameter model will suffice for all practical purposes; with heterogeneous systems, a lumped-parameter model may be adopted if there is a continuous phase and a distributed-parameter model, if there is a disperse phase (in the case of a liquid disperse phase, use may be made of a lumped-parameter model for both phases because perfect mixing may be assumed to exist within each droplet);

— each phase of heterogeneous system may be treated separately, provided the reaction rates are markedly lower than inversion or flooding rates: at high phase velocities their relative velocity must be taken into account or a correction for their interaction should be applied. It is important to stress that changes in the flow pattern(s) of a system may necessitate appropriate changes in the type of model. In turn, the type of model has a direct bearing on the form of equations used in a mathematical description.

Finite equations are usually employed in the mathematical specification of steady-state (stationary) conditions in entities treated as lumped-parameter systems (an apt example is a well-stirred tank reactor). These equations are also used in mathematical descriptions for more complex systems to establish stationary relations between the various parameters.

Ordinary differential equations are used in mathematical descriptions of

the nonsteady-state (dynamic) conditions in lumped-parameter systems, and also steady-state conditions in distributed-parameter systems in which the parameters depend only on one space coordinate. In the former case, the independent variable is time, and in the latter, it is position (coordinate). It should be noted that the mathematical models of reactors differing in physical implementation may have much in common or even be identical in regard to mathematical symbolism. For example, this applies to the dynamic models of well-stirred batch reactors and the stationary models of plug-flow reactors. From the identity of mathematical specification one may conclude that optimum solutions must likewise be identical, although different implementations may be used to realize optimum conditions in these cases. An important feature about mathematical specifications using ordinary differential equations is that initial conditions must be known.

Partial differential equations are used in mathematical descriptions for the dynamic behaviour of distributed-parameter systems or the steady-state behaviour of systems in which the parameters are distributed in more than one coordinate. In the general case, the solution of partial differential equations in the nonsteady-state case requires knowledge of conditions specified by time functions in addition to initial conditions. In the steady-state case, only initial conditions need be specified, and these may be position-dependent.

The mathematical modeling of systems decribed by differential equations may sometimes present a formidable computational problem. This is why, instead of differential equations, one uses a system of finite equations to describe the behaviour of a system. In such a case, a continuous distributed-parameter system is replaced with discrete lumped-parameter systems arranged in a cascade. In terms of mathematical formalism, this reduces to replacing differential equations with difference equations. As regards systems described by ordinary differential equations, a set of finite difference equations is used. For systems described by partial differential equations, use is made of difference-differential equations.

Model-solving algorithms. Most often, the objective of such an algorithm is to solve the equations making up a mathematical description.

Naturally, no algorithm need be developed in simple cases where the equations can be solved analytically. On the other hand, if a mathematical description is a set of finite and differential equations, the applicability of the mathematical model will substantially depend on whether an effective algorithm can be developed. This is especially true of cases where a given model is part of a larger (say, an optimizing) algorithm. In such cases, resort is usually made to analog and digital computers. In fact, computers are the only tools for handling complex problems of mathematical modeling and, the more so, optimization where the equations of a mathematical description are, as a rule, used repeatedly.

The mathematical model of a system described by not too complex differential equations can be set up on an analog computer. Yet, by far

the most versatile tool for solving mathematical models is the digital computer. With a digital computer, a numerical algorithm is needed in order to solve the equations of the mathematical description.

Existing numerical analysis methods are applicable to a wide range of problems involving mathematical models. Yet, in some cases the application of the general methods of numerical analysis may run into difficulties, namely (1) when solving a system of finite nonlinear equations in a great number of variables; (2) when integrating ordinary differential equations under boundary conditions; (3) when integrating partial differential equations.

At present, numerical analysis is lacking general methods for handling the above problems. This is why in developing a model-solving algorithm in each particular case one should utilize the special features of the problem at hand. A good deal of help may come from knowledge of the physical aspects of the solution, as this may suggest acceptable initial approximations for iterative procedures or an efficient model-solving algorithm. An example is the plate-by-plate calculation of distillation columns. In this case, a system of nonlinear equations in a great number of unknowns is solved by iteration.

Sometimes it may so happen that the model-solving algorithm is too elaborate to be handled by a computer at hand. As a way out, the problem may be re-stated so as to simplify its mathematical specification. Unfortunately, this simplification will often impair the accuracy of the mathematical model because some analytical relations may have to be replaced with simpler but, probably, less accurate ones or because some parameters of the prototype system may have to be dropped from the mathematical description.

Testing and adjustment of the model. The first step is to test the selected flow-pattern model for its fit to the system under study. If the experimental response to a step, impulse or sinewave stimulus fits the plot of the solution, this is an indication that the selected model can be used. Experimental responses are obtained on a pilot plant which is geometrically similar to the industrial plant of interest.

In most cases, the existence of stagnation regions and of bypass and recycling streams can be ascertained visually or from examination of the internal arrangement of the reactor and the location of feed inlets and product outlets.

With a well-stirred tank reactor, the goodness of fit can be ascertained by plotting the concentration distribution in the $\ln (1-c_i/c_0)$-*vs*-τ coordinates in response to a step stimulus. If the plot is a straight line, its slope and intercepts will define the parameters of a well-stirred model or of its combinations. This directly stems from the equations examined above.

For a well-stirred model, which is a single-capacitance time-delay element, disturbed by a step stimulus, on the basis of Eq. (I-5) and at $K = 1$, we have

$$y/x = c_i/c_0 = F(\tau) = (1-e^{-\tau/T}) \qquad \text{(II-65)}$$

This equation can be derived directly from the solution of the equation

describing a well-stirred model:

$$dc/d\tau = \frac{1}{\tau_r}(c_0 - c_i) \tag{II-66}$$

where $\tau_r = V/V_q = T$ is the residence time.

Hence, on separating the variables and integration, we get

$$\ln(1 - c_i/c_0) = \frac{1}{\tau_r}\tau \tag{II-67}$$

or

$$c_i/c_0 = 1 - e^{-\tau/\tau_r} \tag{II-68}$$

Thus, in the $\ln(1-c_i/c_0)$-*vs*-τ coordinates, the response of a well-stirred model to a step stimulus should be a straight line whose slope is inversely proportional to the residence time in the well-stirred region, $1/\tau_r$, or $1/m$, where m is the volume of the well-stirred region.

A straightforward estimate of model responses may be made from a plot of the *intensity function*, $\lambda(\tau)$. Physically, the intensity function is a measure of the probability of leaving a reactor for a fluid element that has been present in it for a time τ and will leave it in a time interval $(\tau, \tau + d\tau)$. The intensity function is defined by

$$\lambda(\tau) = -\frac{d}{d\tau}\ln[\bar{\tau}(1 - F(\tau))] \tag{II-69}$$

For a well-stirred model $\lambda(\tau)$ must be constant because the probability that a fluid element will leave such a system is independent of its history. With a plug-flow model, the fact that all fluid elements leave the reactor at the same instant, $\bar{\tau} = V/V_q$, is a certainty, and so the plot of the respective intensity function is a straight-line segment parallel to a coordinate axis and drawn from a point $\theta = 1$ where $\theta = \tau/\bar{\tau}$ on the x-axis (Fig. II-9).

Plots of the intensity functions for arbitrary streams without an appreciable nonlinearity in the average age distribution curves fall between the two mutually perpendicular straight lines representing the λ-functions for ideal systems, as shown in Fig. II-9. The curves are rising because the probability that a given fluid element will leave the reactor increases with its residence time.

For the same reason, a system with stagnation regions will show a rise in the λ-function, just as the main part of the stream is leaving the reactor. After that, the probability of leaving the reactor for the fluid elements will decrease because they are

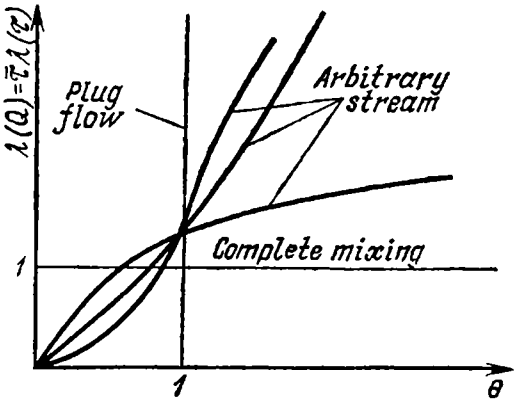


Fig. II-9. Intensity function *versus* dimensionless time for various flow patterns

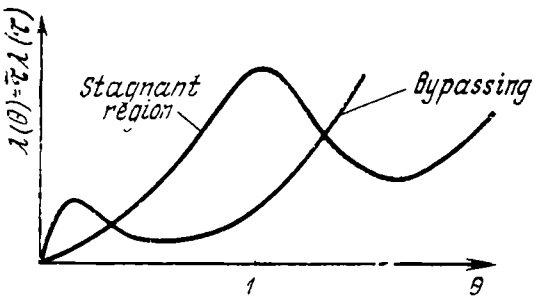


Fig. II-10. Intensity function *versus* dimensionless time for systems with a stagnant region and bypassing

mostly located in the stagnation regions. In other words, the λ-function will not rise without bound; on passing through a maximum, it will take a downward turn (Fig. II-10). With time, the fluid elements in the stagnation regions will gradually leave the system, too. Again, their probability of leaving the system will increase with time. Thus, on passing through a minimum, the λ-function will again rise without bound.

The character of the intensity function for streams with a bypass can be explained in a similar way. In comparison with the previous case, there is only a change in the relative size of the bypass and stagnant parts of the system. This is readily seen from the plot of the respective λ-function in Fig. II-10. A major advantage of intensity-function plots is that they establish the existence of stagnant regions in a system in a simple and straightforward manner.

For reactors represented by models with one or several recycle circuits and well-stirred tanks, the residence time distribution functions can conveniently be found by means of Markov analysis.[5, 6] The matrix of transition probabilities which is governing in this method, fully describes such a model. It is an easy matter to find the matrix determinant for the extreme condition of reactor operation (perfect mixing and plug flow). For perfect mixing:

$$K = \begin{bmatrix} 1-\tau_r \Delta\tau & \tau_r \Delta\tau \\ 0 & 1 \end{bmatrix} \qquad \text{(II-70)}$$

where det K tends to unity and $\Delta\tau$ is the incremental change in $\tau_r = V/V_q$. At small values of $\Delta\tau$, the determinant of matrix (II-70) tends to unity.

A plug-flow model may be visualized as a cascade of m well-stirred single tanks, with m tending to infinity and with the system volume held constant. Therefore

$$K = \begin{bmatrix} 1-\frac{\tau_r}{m}\Delta\tau & \frac{\tau_r}{m}\Delta\tau & 0 & \cdots & \cdots \\ 0 & 1-\frac{\tau_r}{m}\Delta\tau & \frac{\tau_r}{m}\Delta\tau & \cdots & \cdots \\ & & & \cdots & \cdots \\ & & & \cdots & \cdots \\ & & & 1-\frac{\tau_r}{m}\Delta\tau & \frac{\tau_r}{m}\Delta\tau \\ & & & 0 & 1 \end{bmatrix} \qquad \text{(II-71)}$$

Matrix (II-71) is a diagonal one. Therefore, with a small value of $\Delta\tau$ and with m tending to infinity, its determinant K will tend to zero. For inter-

mediate cases, $1 > K > 0$. Thus, the determinant of the transition probability matrix may well serve as a mixing efficiency criterion. This criterion gives an estimate of the versatility of a given model because it defines the width of the residence time distribution function spectrum.

A plot of the determinant of a transition probability matrix for a two-recycle model of variable-structure stirred reactors is shown in Fig. II-11.[5, 6] As should be expected, a variable-structure model covers a wide spectrum

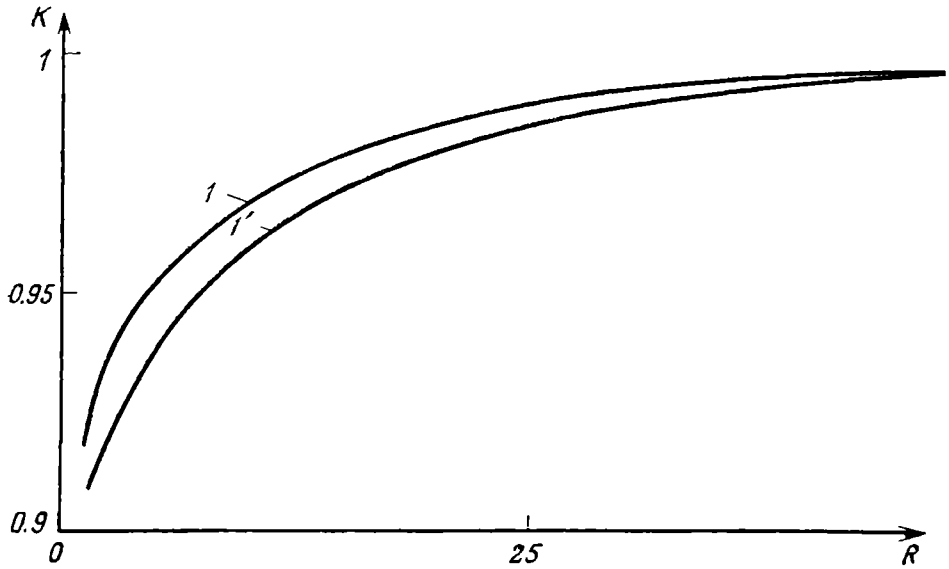


Fig. II-11. Mixing efficiency criterion for stirred reactors described by a two-circuit recycle model, as a function of the recycle-to-inlet stream ratio (R) and locations of inlet and outlet

1 — inlet and outlet at top of reactor; *1'* — inlet at top, outlet at bottom of reactor

of residence time distribution functions for stirred reactors (the determinant ranges from 1 to 0.9), which is an indication of its versatility. The sensitivity of this criterion to changes in reactor parameters, such as the location of the agitator, inlet and outlet, is an indication that it will be as sensitive to stagnant regions and short-circuiting which are not reflected in Péclét numbers.

The two criteria may conveniently be compared by applying them to a cascaded system with direct and recycled streams, which has the widest spectrum of residence time distribution functions. Figure II-12 shows changes in the values of the mixing efficiency criterion K and the Péclét number with the number m of tanks and the recycle fraction, α. As an example, let us find both criteria for a reactor approximated by a model containing ten single tanks and with a recycle fraction of $\alpha = 1.6$. The Péclét number is 4.8, and the proposed mixing efficiency criterion is 0.97. Both criteria show that the model in question approaches perfect mixing very closely.

Thus, the mixing efficiency criterion is no less universal than the Péclét number, as it applies to a wide range of reactors, from columns (represented by a cascaded model) to stirred reactors (represented by a recycling model).

Since in developing a mathematical model, approximate values of some model parameters are used, the problem of model adjustment inevitably arises. Obviously, this problem can readily be solved for an existing process, although a good fit can be secured through the use of physical models which simulate the basic physical relationships of the prototype system on a relatively small scale. If a given mathematical model adequately represents physical models differing in scale (say, an experimental and pilot plant), it will be reasonable to assume that it will also fit a full-scale industrial plant, at least as regards its dominant properties.

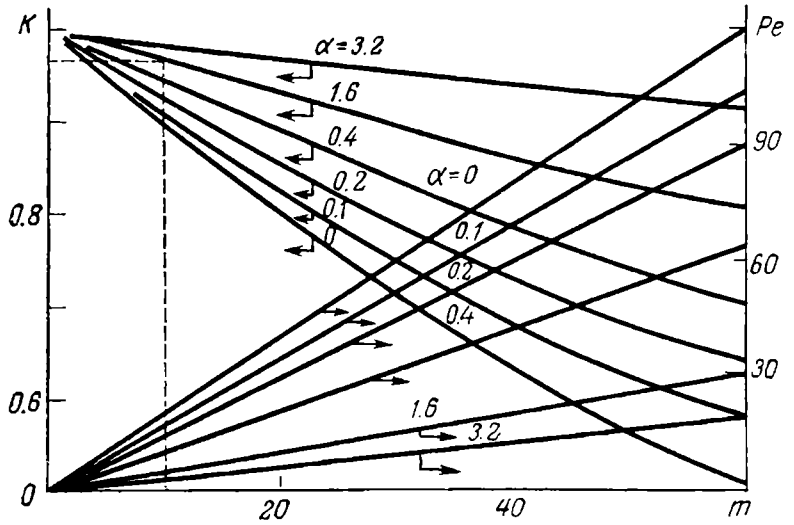


Fig. II-12. Mixing efficiency criterion, $K = f(m)$, and Péclét number, $\mathrm{Pe} = \varphi(m)$ for columns described by a cascade model with direct and recycle streams, as a function of the number of tanks, m, and recycle fraction, α

Before a mathematical model can be adjusted on the basis of measurements made on the process itself or on a physical model, it is important to test the model's adequacy. Let, in the general case, a mathematical model have m parameters whose values cannot be specified *a priori*. Assume also that in an investigation of a real process, only i process variables are observable. Then the model's adequacy may be tested in terms of the following function:

$$\Phi = \sum_{i=1}^{m} \alpha_i (\xi_i - \bar{\xi}_i)^2 \qquad \text{(II-72)}$$

where ξ_i is the value of a model variable, $\bar{\xi}_i$ is the value of the same variable directly measured on the prototype system and α_i is the weight.

Weights may be assigned to the variables from considerations of their importance to the subsequent use of the mathematical model. Thus, for a mathematical model developed to estimate the effect of separation conditions on the characteristics of end products, the highest weights should be assigned to the variables representing these end-product characteristics in the model.

Obviously, the greater the number of observables in Eq. (II-72), the better the test of the model's adequacy.

On the other hand, the function Φ may be treated as a function of a number n of model parameters λ_e and a number p of variables ν_k which describe the external conditions of the process. Mathematically, model adjustment can be stated as a problem of estimating a set of n model parameters that would minimize the function Φ over the entire range of values accessible to the variables ν_k. The variables ν_k may apply to external conditions in a wider sense than it is usually adopted in modeling practice (for example, these may be the number of plates in a column, its diameter, plate geometry, etc.).

The function Φ may be minimized by any one of methods used in finding a maximum or a minimum value for a function of many variables (see p. 135). In principle, it is admissible to estimate model parameters for any one set of variables ν_k ($k = 1, \ldots, n$). Then the minimum value of Φ will be a quantitative estimate of the mathematical model's adequacy.

Of course, for another set of external conditions the function Φ may have an entirely different value, even with the same set of model parameters. Generally, the minimum value of Φ for another set of external conditions will correspond to a different set of model parameters. If, within the range of likely changes, the difference in model parameter values between different sets of external conditions is small, the model may be used to interpolate the properties of the prototype system into that range. In fact, a model can even be extrapolated beyond that range, if the function Φ changes but little within the observed range of changes in the external conditions.

It is important to note that model adjustment presents a fairly complex computational problem which can be tackled by computers of an appreciable capacity.

Example II-2. Identify the model which will fit the reactor whose residence time distribution curve is plotted in Fig. II-1.

Solution. To begin with, find the Péclét number for the distribution curve, $\mathrm{Pe} = wL/D_L$. This can be done by finding the sample variance s^2, using Eqs. (II-7) and (II-6):

$$\sum f(x_i) = \sum c_i = 3+5+5+4+2+1 = 20$$

$$\sum x_i f(x_i) = \sum \tau_i c_i = (5\times 3)+(10\times 5)+ \ldots +(30\times 1) = 300$$

$$\sum x_i^2 f(x_i) = \sum \tau_i^2 c_i = (25\times 3)+(100\times 5)+ \ldots +(900\times 1) = 5450$$

Hence,

$$s_\tau^2 = \frac{\sum x_i^2 f(x_i)}{\sum f(x_i)} - \left[\frac{\sum x_i f(x_i)}{\sum f(x_i)}\right]^2 = \frac{5450}{20} - \left(\frac{300}{20}\right)^2 = 46$$

According to Eq. (II-8), in dimensionless units we have

$$s^2 = s_\tau^2/(\bar{\tau})^2 = 46 \div (15)^2 = 0.204$$

On the basis of Eq. (II-30), the value of $1/\mathrm{Pe} = D_L/wL$ is

$$s^2 = 2D_L/wL = 0.204$$

whence

$$D_L/wL = 0.102$$

and

$$\mathrm{Pe} = wL/D_L = \text{approx. } 10$$

From the Péclét number it is seen that the reactor lies halfway between a well-stirred and a plug-flow model.

Example II-3. The residence time distribution of a tracer has been obtained for a laboratory reactor, using a step stimulus (Fig. II-13). Identify the reactor model, assuming that the feed stream is a solution of salt in distilled water injected as a step change.

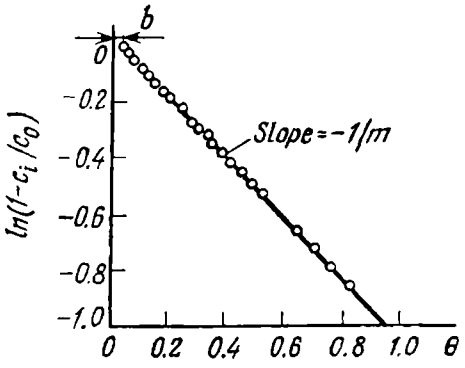


Fig. II-13. Residence time distribution of a tracer material in a laboratory well-stirred reactor

The reactor is a cylindrical vessel 330 mm deep and 100 mm in diameter, with a slightly spherical bottom. The inlet is located 150 mm above the bottom, and the outlet is at the top of the reactor. The agitator is arranged 125 mm above the bottom. The stream velocity is 61.4 $\mathrm{cm^3/min}$, and the agitator speed is 156 $\mathrm{min^{-1}}$.

Solution. To begin with, we shall select a model, then test it for adequacy.

Model selection. On the basis of observed data presented in Fig. II-13, we assume that the reactor should approach very closely a well-stirred model. Since the mixing efficiency varies with agitator speed and fluid velocity, it may be further assumed that there will be a small plug-flow region and a stagnation zone. Therefore, a hybrid well-stirred model should be chosen.

Test for adequacy. Because of a step stimulus, we shall use Eq. (II-43) under the following conditions: $k = 0$, $V_1 = V_4 = V$, $V_2 = V_3 = 0$, $b_2 = b_3 = d_1 = 0$, $b_1 = b$, $m+b+d_2 = 1$.

Then from Eq. (II-43) we find

$$\ln(1-c_i/c_0) = -(1/m)(\theta-b)\,\nu(\theta-b)$$

From the experimental plot of Fig. (II-13), the model parameters are: $m = 0.952$, $b = 0.02$, and $d = 0.03$.

Example II-4. The plot of Fig. II-14 shows the residence time distribution for a tracer in a fluidized bed. Identify the model representing the fluidized bed, assuming that the process system is an air-nitrogen mixture passed through the fluidized bed of a butane hydrogenation catalyst. Nitrogen is injected as an upward step, and the mixing is observed at room temperature. The reactor (column) is 135 mm in diameter. The ratio of bed thickness to reactor diameter is 5 to 1; the average size of catalyst grains is 310 μm.

Solution:

(a) *Model selection.* The inclined straight line in the plot of Fig. II-14 suggests the existence of a well-stirred region. The horizontal line might be interpreted as an indication of a plug-flow region and short-circuiting. Since, however, the gas inlet and outlet are located at the opposite ends of the column, short-circuiting is practically ruled out. Hence, we choose a model in which a well-stirred region and a plug-flow region are arranged in series (see Table II-2).

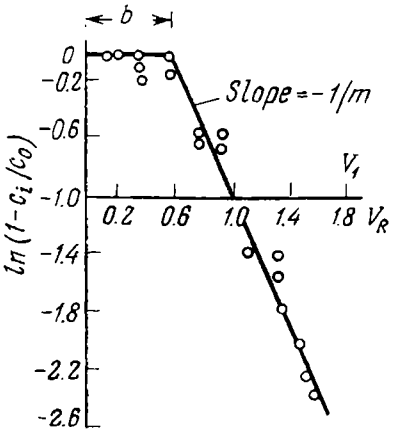


Fig. II-14. Residence time distribution of a tracer material in a pilot fluidized-bed reactor

(b) *Test for adequacy.* Because of a step stimulus, we shall use Eq. (II-43) under the following conditions: $k = 0$, $V_1 = V_4 = V$, $V_2 = V_3 = 0$, $b_1 = b$, $b_2 = b_3 = d_1 = d_2 = 0$.

From Eq. (II-43) we obtain

$$\ln(1 - c_i/c_0) = -(1/m)(\theta - b)\,\nu(\theta - b)$$

From the plot of Fig. II-14, the model parameters are: $m = 0.4$, $b = 0.6$.

Example II-5. The plot of Fig. II-15 shows the residence time distribution of a tracer in a stationary catalyst bed. Identify the model, assuming that the process system consists of hydrocarbons in a stationary bed of desulphation catalyst. The tracer (gas labelled with radiocarbon, C^{14}) is injected as a step disturbance.

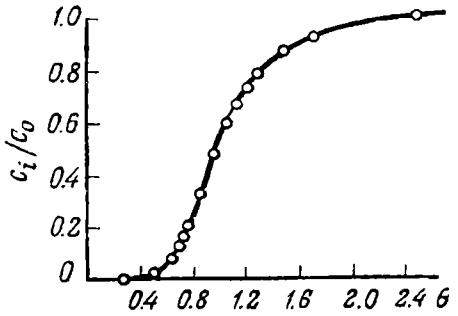


Fig. II-15. Residence time distribution of a tracer material in the stationary catalyst bed of a pilot reactor

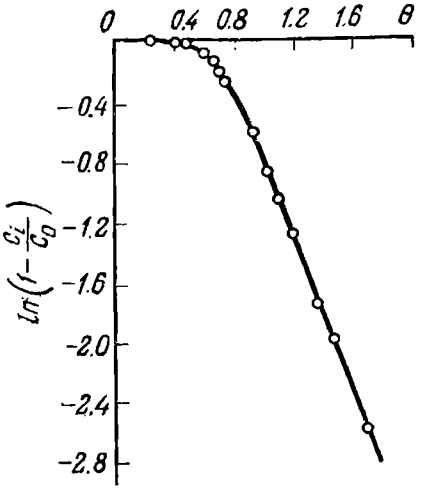


Fig. II-16. Residence time distribution of a tracer material in the stationary bed of a pilot reactor in $\ln(1 - c_i/c_0) - \theta$ coordinates

Solution:

(a) *Model selection.* From the $\ln(1 - c_i/c_0)$-*vs*-θ plot it is seen that there is no linear relationship. Therefore, a well-stirred model cannot be selected for the top portion of the plot. Stationary beds are best approximated with a dispersion or a cascade model. We choose a cascade model.

(b) *Test for adequacy.* At $k = 0$, from Eq. (II-54) we find that $m = 11$.

Example II-6. The following exit concentrations of a tracer have been observed after the imposition of a unit impulse (delta function) stimulus:

Time, min	0	2.5	5.0	7.5	10.0	12.5	15.0	17.5
Tracer concentration, g/m³	0	1.5	3.0	4.5	5.0	5.2	5.0	4.5
Time, min	20.0		22.5	25.0	27.5	30.0	32.5	35.0
Tracer concentration, g/m³	4.0		4.0	2.0	1.0	0.5	0.2	0

The break point is at $a = 35$ min. Determine the mean residence time and the number m of well-stirred tanks on the condition that the process is approximated by a cascade model.

Solution. (1) To begin with, find the first moment for the distribution function from observed data, using Eq. (II-13):

$$M_1^E = \frac{\sum_{i=1}^{n} \tau_i c_i}{\sum c_i} = \frac{(2.5\times 1.5)+(5.0\times 3.0)+(7.5\times 4.5)+(10.0\times 5.0)}{1.5+3.0+4.5+5.0+5.2+5.0+4.5+4.0+3.0+2.0+1.0+0.5+0.2}$$
$$+\frac{(12.5\times 5.2)+(15.0\times 5.0)+(17.5\times 4.5)+(20.0\times 4.0)+(22.5\times 3.0)}{1.5+3.0+4.5+5.0+5.2+5.0+4.5+4.0+3.0+2.0+1.0+0.5+0.2}$$
$$+\frac{(25.0\times 2.0)+(27.5\times 1.0)+(30.0\times 0.5)+(32.5\times 0.2)}{1.5+3.0+4.5+5.0+5.2+5.0+4.5+4.0+3.0+2.0+1.0+0.5+0.2}$$
$$= 14.4 \text{ min}$$

(2) Find the second moment of the distribution function from observed data by Eq. (II-13):

$$M_2^E = \frac{\sum_{i=1}^{n} \tau_i^2 c_i}{\sum_{i=1}^{n} c_i} = \frac{(2.5^2\times 1.5)+(5.0^2\times 3.0)+(7.5^2\times 4.5)+(10.0^2\times 5.0)}{1.5+3.0+4.5+5.0+5.2+5.0+4.5+4.0+3.0+2.0+1.0+0.5+0.2}$$
$$+\frac{(12.5^2\times .5.2)+(15.0^2+5.0)+(17.2^2\times 4.5)+(20.0^2\times 4.0)+(22.5^2\times 3.0)}{1.5+3.0+4.5+5.0+5.2+5.0+4.5+4.0+3.0+2.0+1.0+0.5+0.2}$$
$$+\frac{(25.0^2\times 2.0)+(27.5^2\times 1.0)+(30.0^2\times 0.5)+(32.5^2\times 0.2)}{1.5+3.0+4.5+5.0+5.2+5.0+4.5+4.0+3.0+2.0+1.0+0.5+0.2}$$
$$= \frac{9934}{39.4} = 252 \text{ min}^2$$

(3) Find the value of x and develop a set of simultaneous equations in two unknowns, m and ε (see p. 113):

$$x = \frac{a}{M_1^E} = \frac{35}{14.4} = 2.43$$

$$\left.\begin{aligned} M_1^M &= \frac{M_1^E}{M_1^E} = 1 \\ M_2^M &= \frac{M_2^E}{(M_1^E)^2} = 1.21 \end{aligned}\right\}$$

The set of simultaneous equations has the form:

$$\left.\begin{aligned} 1 &= \frac{m}{b}\left\{1-(e^{-bx})\left[\frac{(bx)^m}{m!}+\frac{(bx)^{m-1}}{(m-1)!}+\ \ldots\ +\frac{(bx)^2}{2!}+bx+1\right]\right\} \\ 1.21 &= \frac{(m+1)m}{b^2}\left\{1-(e^{-bx})\left[\frac{(bx)^{n+1}}{(m+1)!}+\frac{(bx)^n}{m!}+\ \ldots\ +bx+1\right]\right\} \end{aligned}\right\}$$

where $b = m\varepsilon$; $\varepsilon = \dfrac{M_1^E}{V/V_q}$

On solving the set of equations, we get:

$$m = 4, \quad b = 3.84$$

From $b = m\varepsilon$, we find:

$$\varepsilon = 3.84 \div 4 = 0.96$$

Hence,

$$V/V_q = M_1^E/\varepsilon = 14.4 \div 0.96 = 15 \text{ min}$$

Thus, the mean residence time is $V/V_q = 15$ min, and the number of tanks is $m = 4$.

II-4. PROCESS OPTIMIZATION THROUGH MATHEMATICAL MODELS

Process optimization consists in finding an optimum value for a given function or optimum conditions for a given process.

Before an optimum can be estimated properly, we must choose an *optimization criterion.* This may be a process variable, say, the yield of a product per unit volume of a reactor, a minimum cost of product for a specified output, etc.

On the basis of the optimization criterion, one then develops an *objective* or *return function* which relates the optimization criterion to the dominant parameters. The goal of optimization is to maximize or minimize the objective function, as the case may be.

The problem of optimization occurs in cases where one has to strike a compromise between two or more quantitative characteristics affecting the process variables differently by balancing one against the other(s). For example, the process efficiency may be balanced against throughput, quality against quantity, inventory of products against their sales, productivity against expenditures, etc.

As regards automatically controlled processes or systems, optimization is thought of as consisting of two stages, static and dynamic (see p. 69).

Static optimization has as its goal to develop and realize an optimum model for the process in question. *Dynamic optimization* seeks to develop and realize an optimum control system for the process.

Depending on the nature of mathematical models chosen, different methods of mathematical optimization may be used. Many of them seek to

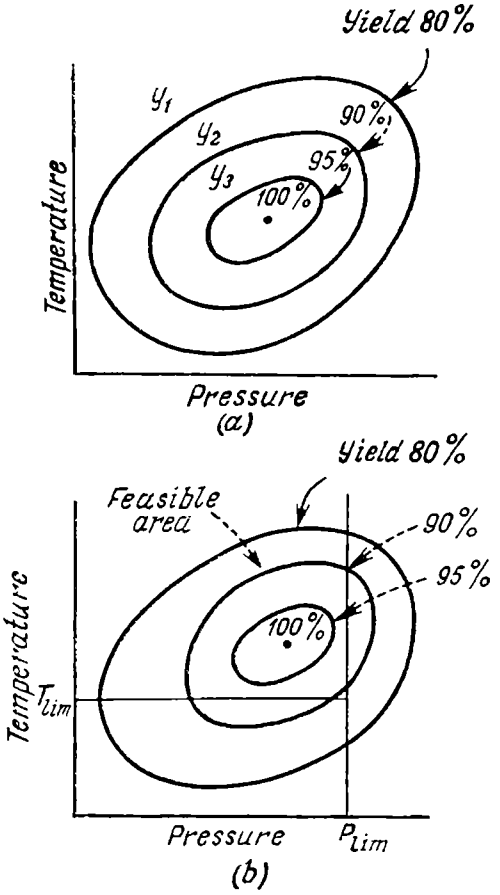


Fig. II-17. Response surface relating product yield to temperature and pressure
(*a*) without constraints; (*b*) with constraints

maximize or minimize the objective function. In response-surface methodology, for example, the objective function is represented as contours lying on a response surface. In the plot of Fig. II-17, the response surface connects the yield of product to temperature and pressure. The contours run through the points at which the objective function (yield of product) has the same value for different values of temperature and pressure.

Different contours never intersect. All contours representing the values of y (yield of product) greater than y_1 (in maximization) or smaller than y_1 (in minimization) fall within the contour representing y_1. The objective function may be specified with or without constraints on some process variables. Figure II-17*b* shows the response surface of an objective function for which the constraints are the limits for changes in temperature T_p and pressure P_p which affect the yield of the product.

The optimization methods most commonly used are listed in Table II-3.

In selecting an optimization method, it is important to envisage the computational difficulties that may arise. It will be a good plan to estimate the position of the optimum for some specific problem, if and where practicable, which involves an analysis of starting and basic relations between the variables. The number of dimensions involved may be reduced by retaining only the most significant variables.

It is preferable to use identical computational set-ups and standard subroutines so as to reduce the amount of computation, and to develop a special program only for objective functions (which may happen, say, in dynamic programming).

Hard and fast rules for problem simplification that would be applicable to all situations cannot be formulated; judgement should be used in each particular case. What follows is only a brief outline of the optimization methods most widely used in chemistry and chemical engineering.

Table II-3

Optimization Methods Used in Chemistry and Chemical Engineering

Method	Application
	Analytical methods
Optimization by direct search for the extremum	Deterministic processes described by differentiable functions
Method of Lagrangian multipliers	Deterministic processes described by differentiable functions with inequality constraints
Calculus of variations	Performance criteria in the form of functionals. Solution of Euler's equation. Multilayer adiabatic reactors. Optimum temperature conditions for reversible exothermal reactions in plug-flow beds; optimum temperature conditions for chemical reactors in the case of constraints on temperature range, etc.
Pontryagin's maximum principle	Wide range of problems, especially in automatic control
	Mathematical programming
Geometric programming	Optimization of algebraic functions
Linear programming	Manufacture of products for maximum return from different raw materials. Optimum utilization of equipment. Transportation problem
Dynamic programming	Multistage processes: distillation, extraction, absorption. Cascaded reactors, multisection adiabatic beds, interacting chain of reactors, etc. Markov processes
	Gradient methods
All forms	Optimization of linear and nonlinear functions with and without linear or nonlinear constraints. Complex chemical-engineering processes. Single and cascaded interacting reactors
	Optimizing by computer control and model adaptation
All forms	Complex chemical-engineering systems
	Statistical optimization
Regression analysis	Nondeterministic systems
Correlation analysis, Brandon method, Box-Wilson method, etc.	Experiment optimization and designs

(A) ANALYTICAL METHODS OF OPTIMIZATION

These are classical methods for maximizing or minimizing a function, used when the function to be optimized is specified analytically and the number of independent variables is limited. With a large number of variables one runs into the curse of dimensionality, and analytical methods become difficult to use. Constraints, too, may curb the usability of analytical methods. Because of this, analytical methods find a limited use in practice. For the reader's convenience Pontryagin's maximum principle will be discussed after the gradient methods.

In seeking an optimum for a problem in which the independent variables are unknown functions, one may use *calculus of variations* (see Table II-3). Then the problem will reduce to maximizing or minimizing a functional of one or a few unknown functions.

In an analytical search for a maximum or minimum value for a continuous objective function, $F(x_1, x_2, \ldots, x_n)$, where $x_1, x_2, \ldots, x_i, \ldots, x_n$ are independent variables, its partial derivatives are set equal to zero

$$\sum_{i=1}^{n} \frac{\partial F}{\partial x_i} dx_i = 0 \qquad \text{(II-73)}$$

Since the differentials dx_i may be chosen independently, then

$$\sum_{i=1}^{n} \frac{dF}{dx_i} = 0 \quad i = 1, 2, \ldots, n \qquad \text{(II-74)}$$

The classical analysis method for a function of a single independent variable, $F(x_1)$, makes it possible to find the coordinates of a maximum (or minimum) from the condition

$$F'(x_1) = 0$$

The kind of the extremum (maximum or minimum) is identified by well-known rules for the second derivative:

$$\left.\begin{array}{llll} \text{if} & F''(x_1) > 0, & \text{then} & \min^+ \\ \text{if} & F''(x_1) < 0, & \text{then} & \max^- \end{array}\right\} \qquad \text{(II-75)}$$

At $F''(x_1) = 0$, the behaviour of $F''(x_1)$ in the vicinity of the point or the higher derivatives should be analysed. If the next higher non-zero derivative is an even-order derivative, an extremum does exist. If, on the other hand, this is an odd-order derivative, there is no extremum. For example, there is neither a maximum nor a minimum for a cubic parabola:

$$y = x^3 \qquad y' = 3x^2 = 0$$
$$y'' = 6x = 0 \qquad y''' = 6 \neq 0$$

If there are more than one variable, the difficulties in finding an extremum become considerable. For a function of two variables, $F(x_1, x_2)$, we have

$$F'_{x1}(x_1, x_2) = 0$$

and

$$F'_{x2}(x_1, x_2) = 0$$

and each pair of values produces a point. As a check on the extremum, the following expression is analysed:

$$\Delta = F''_{x_1, x_1} F''_{x_2, x_2} - (F''_{x_1, x_2})^2 \qquad \text{(II-75}a\text{)}$$

If $\Delta > 0$, an extremum does exist. If $\Delta < 0$, there is no extremum. At $F''_{x_1, x_2} < 0$ there is a maximum. At $F''_{x_1, x_2} > 0$, there is a minimum.

Lagrangian multipliers. This method is ordinarily used when equality constraints are imposed on the variables. If we wish to find the values of $x_1, x_2, \ldots, x_n$ which maximize (or minimize) F subject to $f_i(x_1, x_2, \ldots, x_n) = 0$ ($i = 1, \ldots, m$; $m < n$), then, by the method of Lagrange, an auxiliary function is formed

$$\varphi(x_1, \ldots, x_n, \lambda_1, \ldots, \lambda_m) = F(x_1 x_2, \ldots, x_n) + \sum_{i=1}^{m} \lambda_i f_i(x_1, \ldots, x_n) \qquad \text{(II-76)}$$

where λ_i ($i = 1, \ldots, m$) are undetermined multipliers called Lagrangian multipliers. Then, in order to determine the extremal values of $F(x_1, x_2, \ldots, x_n)$, all that is necessary is to obtain the solution of a system of equations which are set up by equating to zero the derivatives of the function $\varphi(x_1, \ldots, x_n; \lambda_1, \ldots, \lambda_m)$ with respect to all independent variables x_k ($k = 1, \ldots, n$) and with respect to all Lagrangian multipliers, λ_i ($i = 1, \ldots, m$).

This system of simultaneous equations

$$\left.\begin{aligned} \frac{\partial \varphi(x_1, \ldots, x_n, \lambda_1, \ldots, \lambda_m)}{\partial x_k} &= 0 \quad k = 1, \ldots, n \\ \frac{\partial \varphi(x_1, \ldots, x_n, \lambda_1, \ldots, \lambda_m)}{\partial \lambda} &= f_i(x_1, \ldots, x_n) = 0 \end{aligned}\right\} \qquad \text{(II-77)}$$

$$i = 1, \ldots, m$$

has $n+m$ equations from which m Lagrangian multipliers of an auxiliary nature may be dropped and the coordinates of extremal points x'_k ($k = 1, \ldots, n$) may be found. In the general case, there may be several such points, that is, $l = 1, 2, \ldots, n$.

Each constraint adds one more equation, and for each new constraint one more Lagrangian multiplier is introduced. It should be noted that the method of Lagrangian multipliers is also employed as an auxiliary tool in the solution of other classes of problems with equality constraints, for example by variance analysis and dynamic programming. The use of Lagrangian multipliers is especially efficient in programming methods, where they reduce the number of dimensions involved.

Example II-7.[7] Determine the dimensions of an open rectangular tank with a capacity of 1000 m³, which will minimize the surface area of the bottom and walls. The tank volume is $V = lbh$, where l is the length, b is the width, and h is the depth.

Solution. We seek to minimize surface area, that is, the function

$$F(l, b, h) = 2hb + lb + 2hl$$

Constraints. $f(l, b, h) = 0$, that is, $f(l, b, h) = lbh - V$.

The auxiliary function has the form

$$\varphi = (l, b, h, \lambda) = F(l, b, h) + \lambda(lbh - V)$$

or

$$\varphi = (l, b, h, \lambda) = 2bh + lb + 2hl + \lambda(lbh - V)$$

On taking partial derivatives with respect to l, b, h, and λ we get

$$\frac{\partial \varphi}{\partial l} = b + 2h + \lambda bh = 0 \qquad \text{(a)}$$

$$\frac{\partial \varphi}{\partial b} = 2h + l + \lambda lh = 0 \qquad \text{(b)}$$

$$\frac{\partial \varphi}{\partial h} = 2b + 2l + \lambda lb = 0 \qquad \text{(c)}$$

$$\frac{\partial \varphi}{\partial \lambda} = lbh - V = 0 \qquad \text{(d)}$$

Setting these four partial derivatives equal to zero and solving the four equations simultaneously, from Eq. (a) we get

$$\lambda = \frac{-(b + 2h)}{bh} \qquad \text{(e)}$$

Substituting the expression for λ in Eq. (b) and solving it for b, gives $b = 1$. From Eq. (c) we find that $\lambda = -4/b$, and from Eq. (a) it follows that $b = 2h$. Thus

$$V = lbh = (b)(b)(b/2) = b^3/2 = 1000 \text{ m}^3$$

whence $l = 12.6$ m, $b = 12.6$ m, and $h = 6.3$ m.

(B) MATHEMATICAL PROGRAMMING

Geometric programming. This method is applicable to minimizing algebraic expressions of the form

$$F(x_1, x_2, \ldots, x_n) = \sum_{j=1}^{l} C_j P_j(x_1, x_2, \ldots, x_n) \qquad \text{(II-78)}$$

where C_j are positive constants.

$$P_j(x_1, x_2, \ldots, x_n) = \prod_{i=1}^{n} x_i^{a_{ij}} = x_1^{a_{1j}}, x_2^{a_{2j}}, \ldots, x_n^{a_{nj}} \qquad \text{(II-79)}$$

where a_{ij} are real numbers.

Geometric programming is based on the theorem of the mean, according to which the arithmetic mean of positive numbers is always greater than or equal to their geometric mean, that is

$$(1/2)y_1+(1/2)y_2 \geqslant (y_1y_2)^{1/2} \tag{II-80}$$

On defining the values of δ_i as

$$\delta_1+\delta_2+ \ldots +\delta_m = 1 \tag{II-81}$$

Equation (II-80) may be generalized as follows

$$\delta_1y_1+\delta_2y_2+ \ldots +\delta_my_m \geqslant y_1^{\delta_1}y_2^{\delta_2} \ldots y_m^{\delta_m} \tag{II-82}$$

According to inequality (II-82) we may write

$$M = M_1+M_2+ \ldots +M_m = \delta_1\left(\frac{M}{\delta_1}\right)+\delta_2\left(\frac{M}{\delta_2}\right)+ \ldots +\delta_m\left(\frac{M}{\delta_m}\right)$$
$$\geqslant \left(\frac{M_1}{\delta_1}\right)^{\delta_1}\left(\frac{M_2}{\delta_2}\right)^{\delta_2} \ldots \left(\frac{M_m}{\delta_m}\right)^{\delta_m} \tag{II-83}$$

where $M_1, M_2, \ldots, M_m$ are positive numbers, and $\delta_1, \delta_2, \ldots, \delta_m$ are found from Eq. (II-81).

In the general case, the number M_j is a function of many variables, $x_1, x_2, \ldots, x_n$. The left-hand side of Eq. (II-83) is a function of only the variables x_i ($i = 1, 2, \ldots, n$), and the right-hand side is a function of only the variables $-x_i$ ($i = 1, 2, \ldots, m$) and δ_j ($j = 1, 2, \ldots, m$).

Let now M_j be

$$M_j = C_jP_j(x_1, x_2, \ldots, x_n) = C_j(x_1)^{a_{1j}}, (x_2)^{a_{2j}}, \ldots, (x_n)^{a_{nj}} \tag{II-84}$$

where all $x_i \geqslant 0$ ($i = 1, 2, \ldots, n$).

According to Eq. (II-84), the quantity M in Eq. (II-83) is equal to $F(x_1, x_2, \ldots, x_n)$ in (II-78).

Noting (II-84), Eq. (II-83) may be re-written as follows

$$F(x_1, x_2, \ldots, x_n) = \sum_{j=1}^{m} C_j \prod_{i=1}^{n} x_i^{a_{ij}} \geqslant \prod_{j=1}^{m}\left(\frac{C_j}{\delta_j}\right)\left(\prod_{i=1}^{n} x_i^{a_{ij}}\right)^{\delta_i} \tag{II-85}$$

The function $F(x_1, x_2, \ldots, x_n)$ is a minimum only if (II-85) turns to an equality, and this can happen on the condition that

$$\sum_{j=1}^{m} a_{ij}\delta_j = 0 \quad (i = 1, 2, \ldots, n) \tag{II-86}$$

Thus, the numbers b_j should satisfy the conditions (II-81) and (II-86). In other words, the minimization of the function $F(x_1, x_2, \ldots, x_n)$ reduces to finding the values of δ_j for the function u

$$u = \prod_{j=1}^{m}\left(\frac{C_j}{\delta_j}\right)\left(\prod_{i=1}^{n} x_i^{a_{ij}}\right)^{\delta_j} \tag{II-87}$$

that will satisfy Eqs. (II-81) and (II-87), that is

$$\delta_1+\delta_2+ \ldots +\delta_m = \sum_{j=1}^{m} \delta_j = 1$$

$$a_{i1}\delta_1+a_{i2}\delta_2+ \ldots +a_{im}\delta_m = \sum_{j=1}^{m} a_{ij} = 0$$

$$i = 1, 2, \ldots, m$$

Then Eq. (II-85) turns to an equality so that $u = F^*$, where F^* is the minimum value of $F(x_1, x_2, \ldots, x_n)$.

A major advantage of geometric programming is that it reduces the complex problem of optimizing a nonlinear relation to a solution of a system of simultaneous algebraic equations. Besides, once the numbers δ are found, the minimum value of the optimality criterion can directly be determined without having to compute the variables that lead to this minimum.

Example II-8.[8] Using the method of geometric programming, find the number of filtration cycles for a volume V_t that will minimize the total filtration time.

The time per filtration cycle is

$$\theta = \theta_f+\theta_w+\theta_d$$

where θ_f is the filtration time, θ_w is the washing time, and θ_d is the discharge and clean-up time.

In the case of filtration at constant pressure, the time required to filter a volume V_t is given by

$$n\theta = nKV_q^2$$

where $V_q = V_t/n$ is the filtrate volume per cycle, n is the number of cycles, and K is a proportionality constant.

If the volume of washing water is proportional to V_q, the washing time will be

$$n\theta_w = \beta nKV_q^2$$

where β is a proportionality constant.

The discharge and clean-up time is $n\theta_d$.

Thus, the total time needed to filter the volume V_t is

$$\theta_t = (KV_t^2+\beta KV_t^2)\frac{1}{n}+\theta_d n$$

To solve the optimization problem, determine the number of cycles, n, which will minimize θ_t.

Solution. On setting $A = KV_t^2+\beta KV_t^2$, the time per volume V_t will be

$$\theta_t = An^{-1}+\theta_d n$$

Form the function u

$$u = (A/\delta_1)^{\delta_1}(\theta_d/\delta_2)^{\delta_2}$$

subject to the constraints

$$\left.\begin{aligned} \delta_1+\delta_2 &= 1 \\ (-1)\delta_1+(+1)\delta_2 &= 0 \end{aligned}\right\}$$

Solving these equations simultaneously for δ_1 and δ_2 gives

$$\delta_1 = \delta_2 = {}^1/_2$$

Thus, the minimum filtration time is

$$\theta_{f\,\min} = u = (4A\theta_d)^{1/2} = 2(A\theta_d)^{1/2}$$

Besides, the equality $\delta_1 = \delta_2$ implies that in order to minimize the filtration time, the discharge and clean-up time, θ_d, should be equal to the sum of the filtration and washing times, $\theta_f+\theta_w$. The number of cycles, n, is found, from this condition, that is:

$$(A\theta_d)^{1/2} = An_{opt}^{-1} = \theta_d n_{opt}$$

$$n_{opt} = (A/\theta_d)^{1/2}$$

Linear programming. This is a method of solving problems in which an objective function must be maximized or minimized when considering certain constraints. The objective function is a linear one of the form

$$F = c_1x_1+c_2x_2+ \ldots +c_nx_n \tag{II-88}$$

and the constraints are linear inequalities of the form

$$a_{i1}x_1+a_{i2}x_2+ \ldots +a_{im}x_m \geqslant b_i \tag{II-89}$$

$$x_1, \ldots, x_n \geqslant 0 \tag{II-90}$$

where x's are the variables or parameters to be optimized.

The class of problems solved by the linear programming technique is exemplified by the following types:

(1) A manufacturer wishes to maximize the profit associated with making different products from different raw materials.

(2) A manufacturer wishes to maximize the utilization of his facilities or resources. Suppose he wishes to make N_1 units of product P_1 and N_2 units of product P_2 in a time τ. These products are manufactured by two machine centres, A and B, differing in both output and cost. The production must be organized so as to minimize maintenance costs.

(3) A manufacturer wishes to minimize his transportation costs (the transportation problem). Products manufactured at points A_1 and A_2 are to be moved in the most economical manner to consumption centres, B_1, B_2 and B_3. The transportation costs must be minimized within the factory's constraints (say, the fulfilment of the plan).

Several computational procedures are available to linear programming (graphic, algebraic and simplex). They are all iterative processes, the same basic steps being used over and over again until the best solution is found. This is why they can readily be adapted to implementation on a computer.

In the graphic method of linear programming, involving two-dimensional problems the constraints are plotted as straight lines to define the feasible solution area, then a series objective function lines are drawn (in fact, the objective function line appears to be moved parallel to itself, see Fig. II-18) to determine the farthest point from the origin where the objective function is a maximum. In *n*-dimensional problems, the objective function is a hyperbola and the constraint inequalities define a convex polygon which appears to move parallel to itself as the objective function is optimized. The solution (if unique) is always at the vertex and fills an edge of the polygon.

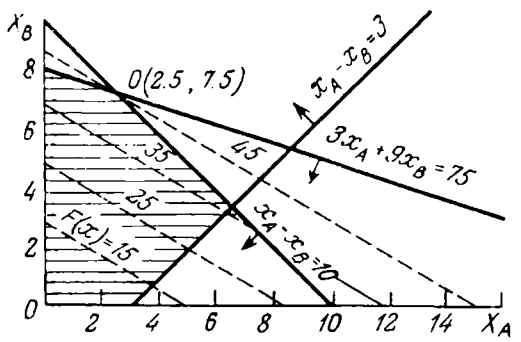


Fig. II-18. Graphical method of linear programming

Example II-9.[9] Suppose two products, *A* and *B*, are manufactured. The contribution has been computed to be 3 roubles from product *A* and 5 roubles from product *B*. It is sought to maximize the total contribution and to optimize the number of products *A* and *B* made, x_A and x_B. This is a two-dimensional problem which we shall solve by the graphic method of linear programming.

The objective function may be set up as

$$F(x) = 3x_A + 5x_B$$

It is subject to the following linear constraints:

— an inequality constraint on the conduct of the process:

$$x_A - x_B \leqslant 3$$

— an inequality constraint on the total number of products *A* and *B* manufactured:

$$x_A + x_B \leqslant 10$$

— an inequality constraint on the supply of raw materials:

$$3x_A + 9x_B \leqslant 75$$

A further constraint is

$$x_A, x_B \geqslant 0$$

Solution. Referring to the plot of Fig. 11-18, the solid lines represent the various constraint inequalities, and the dashed lines are the objective function lines. The striped area enclosed by the constraint lines is the feasible solution area — it contains all possible combinations of products satisfying all the original inequalities. The objective function is maximized at the farthest point in the feasible solution area, point *0*, lying on the maximum contribution line. Since this point is still within the feasible solution area, it satisfies the constraint inequalities and represents the most profitable

combination of products. Thus, the optimum solution is to make $x_A = 2.5$ units of product A and $x_B = 7.5$ units of product B, so that the total contribution is 45 roubles.

Dynamic proramming. This method is a multistage process of decision making in which the decisions are made in a certain sequence, such that the state of the system depends on the immediately preceding decision and is independent of all other decisions made before.

Dynamic programming is based on Bellman's *principle of optimality* which states that whatever the initial state(s) and initial decision(s) may be, the remaining decisions must constitute an optimal policy with respect to the state resulting from the first decision.[10, 12]

In other words, if a stream is subject to changes in each stage of a process, failure to maintain optimum conditions for this stream in the last stage (irrespective of what they were in the previous stages) means that the operating conditions of the entire multistage process will not be optimal, either.

Thus, dynamic programming consists in breaking down the process of interest into steps or stages in time or space and in finding operating conditions for each step or stage which will maximize the performance (say, the profit) at this and all the steps or stages that lie ahead, no matter what the state of the incoming stream may be. As a rule, the analysis starts at the last step or stage of the process, and the optimum conditions for the process are found stage by stage, working backwards.

The unit step or stage may be a unit of time (a minute or an hour), a piece of equipment (a plate in a distillation column or a reactor in a cascade). In any case, the step or stage is a mathematical abstraction applied to present the continuous variable of interest in discrete form. The state of the system is characterized by a set of state variables applicable to any one of the process steps or stages.

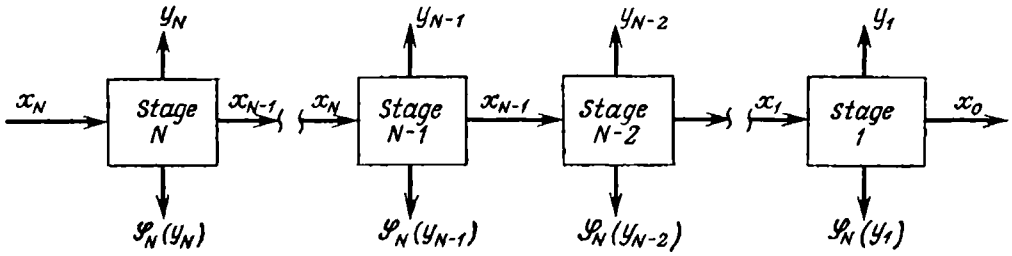


Fig. II-19. Explaining dynamic programming

Figure II-19 shows a multistage process, where N is the total number of stages. Each stage is described by a state variable x and has inputs and outputs of its own. At each stage, a decision is made to maximize the state variable, x, by manipulating the input variables, y. The gain, or return, generated by each decision at the Nth stage is given by $\varphi_N(y_N)$.

The basic equation of dynamic programming is a functional equation of the form

$$F_N(x) = \max_{y_{N-1}} [\varphi_N(y_N) + F_{N-1}(x - y_N)] \qquad \text{(II-91)}$$

where $F_N(x)$ is the function being optimized in an N-stage process, N is the number of process stages that lie ahead, x is the state variable at an Nth stage. The symbol "max" indicates that maximization is carried out by selecting the value of y_N in the range from 0 to x. The term $F_{N-1}(x-y_N)$ is the objective function for the succeeding $(N-1)$ stages after the decision on the value for y_N is made.

Let the optimum selected value of y_N be y_N^*. If the state of the system changes from x at stage N to $x-y_N^*$ at stage $(N-1)$, then the optimum value of the function observed after passing through the $N-1$ remaining stages will be $F_{N-1}(x-y_N^*)$. This is the resultant gain generated upon completion of the $N-1$ remaining stages, starting with state $x-y_N^*$, and may be found from the equation

$$F_{N-1}(x-y_N^*) = \max_{y_{N-1}} [\varphi_N(y_{N-1})+F_{N-2}(x-y_N^*-y_{N-1})] \qquad \text{(II-92)}$$

As is seen, the choice of y_{N-1} is limited to the range of values from 0 to $x-y_N^*$, because the starting state variable has been decreased to $x-y_N^*$ due to the selection of y_N^* at the Nth stage. The decision strategy is expressed by a set of selected values of y_i which are the terms of Eq. (II-91), where $i = 1, 2, \ldots, N$. This system yields the solution of the functional equation. The optimum decision strategy is expressed by a system of functions y_i which maximize the right-hand side of Eq. (II-91), namely $y_1^*, y_2^* \ldots, y_N^*$ for $i = 1, 2, \ldots, N$.

In many cases it is more important to know the optimum decision strategy than the value of the objective function. In determining the function $F_N(x)$, one obtains a sequence of decisions y_i, or strategy, also as a function of the stage No., i. The first step is to choose the starting state described by the state variable x, after which the first decision is made on $y_N = y_N^*$. The succeeding decisions are taken on the basis of the expression $F_{N-1}(x-y_N^*)$.

Functional equations are usually solved by numerical methods. Very often, this is done with the aid of a computer as follows. To begin with, one finds $F_1(x)$. Then, using this value and Eq. (II-91), the function $F_2(x)$ is found. After that, $F_3(x)$ is found from $F_2(x)$, etc.

The advantages offered by dynamic programming will be clear from the following example. Let there be an N-stage process in which K decisions are taken at each stage (in Fig. II-20 $K = 3$ and $N = 2$). For each alternate

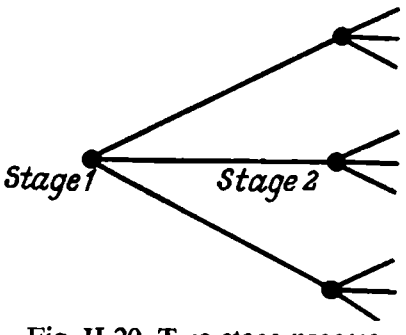


Fig. II-20. Two-stage process

decision that may be made at the Nth stage, there are K alternate decisions that may be made at the $(N-1)$th stage. For each decision made at the $(N-1)$th stage, there are K decisions that may be made at the $(N-2)$th stage, etc. Thus, in order to find an optimum decision, one would have to analyse the number K^N of alternate decisions or courses of action. Although such an analysis is possible in principle, it could hardly be done at high values of K and N, even if one used computers with the highest speed of operation.

Dynamic programming makes unnecessary an analysis of all K^N decisions; each stage is analysed separately, and the best of K decisions is selected for each stage. Thus, with dynamic programming only NK combinations are analysed instead of K^N combinations. At $K = 3$ and $N = 10$, the conventional approach would call for an analysis of $3^{10} \approx 5.9 \times 10^4$ combinations. With dynamic programming, the number is 30. At $K = 3$ and $N = 100$, the conventional technique would involve an analysis of $3^{100} \approx 5.15 \times 10^{47}$ combinations; with dynamic programming, analysis is limited to 300 combinations. Thus, dynamic programming drastically reduces the amount of computations and facilitates the solution of problems.

Among the shortcomings of dynamic programming, the following may be stressed:

(1) The method is used to maximize or minimize a function, but it does not tell how this should be done (that is, how the values of y_N should be selected).

(2) The method becomes complicated in the case of processes with recycling.

(3) The method is of a limited value in the case of a multidimensional process, as the amount of computational work becomes prohibitive.

Example II-10.[13] Using dynamic programming, find the minimum total volume and the volume of each of three continuous stirred tank reactors in an isothermal cascade for a simple first-order reaction. The final fractional conversion is $x_{A3} = 1 - C_{A3}/c_{A0} = 0.9$.

Solution. The material balance (see p. 109) around the reactors numbered 1, 2 and 3 in the direction of stream is as follows

$$\frac{c_{A1}}{c_{A0}} = \frac{1}{1+k\tau_1} \qquad \frac{c_{A2}}{c_{A1}} = \frac{1}{1+k\tau_2} \qquad \frac{c_{A3}}{c_{A2}} = \frac{1}{1+k\tau_3}$$

Starting with the third stage, let us write an expression for $k\tau_3$:

$$k\tau_3 = \frac{c_{A2}}{c_{A3}} - 1 = \frac{c_{A2}}{c_{A0}} \cdot \frac{c_{A0}}{c_{A3}} - 1 = \frac{c_{A2}}{c_{A0}} \cdot \frac{1}{0.1} - 1$$

The expression is plotted as a straight line at the bottom of the plot in Fig. II-21.

For the second reactor, $k\tau_2$ may be defined by

$$k\tau_2 = \frac{c_{A1}}{c_{A2}} - 1 = \frac{c_{A1}}{c_{A0}} \cdot \frac{c_{A0}}{c_{A2}} - 1$$

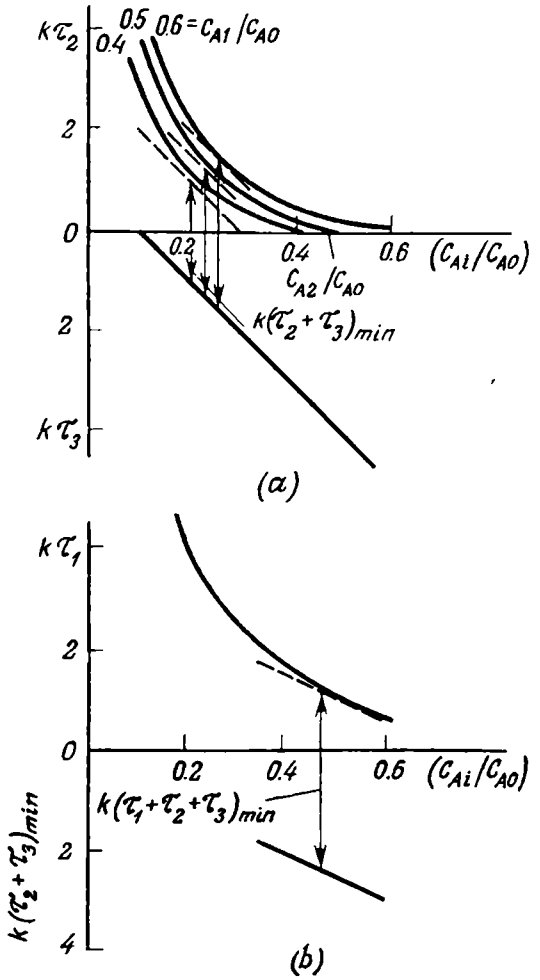


Fig. II-21. Finding the overall minimum volume for an isothermal cascade of reactors

This expression is plotted as a set of hyperbolas at the top of Fig. II-21, with the ratio c_{Ai}/c_{A0} taken as the parameter. The minimum value, $k(\tau_2+\tau_3)_{\min}$, is found graphically (Fig. II-21*a*) as the shortest distance between these curves and the slant straight line.

The minimum value of the objective function, $k(\tau_1+\tau_2+\tau_3)_{\min}$, is found similarly, as the shortest distance between two curves (Fig. II-21*b*), at the respective value of c_{A1}/c_{A0}.

As a result, we have:

$$k(\tau_1+\tau_2+\tau_3)_{\min} = 3.45$$
$$k(\tau_2+\tau_3)_{\min} = 2.30$$
$$k(\tau_3)_{\min} = 1.15$$

and at $\tau_1 = \tau_2 = \tau_3$

$$\frac{c_{A1}}{c_{A0}} = \frac{c_{A2}}{c_{A1}} = \frac{c_{A3}}{c_{A2}} = 0.465$$

(C) GRADIENT METHODS OF OPTIMIZATION

These are numerical methods of the search type. They are universal and well adapted to digital computers, and prove most efficient in most cases where the search is for the extremal values of constrained and unconstrained nonlinear functions, and also when a function is not known analytically altogether. This is why the gradient or search methods are widely used in practical applications.

In essence, these methods reduce to finding the values of independent variables generating a maximum change in the objective function. As a rule, this is achieved by moving along a gradient which is a vector orthogonal to the performance contour surface at a given point.

The various search methods mainly differ in the manner of ascertaining the direction of movement towards the optimum, the length or size of the step, the time of search along the selected direction, criteria for search termination, algorithms, and adaptability to different digital computers.

The technique of the search for extremal values is based on computations which readily ascertain the direction which ensures the fastest approach to the optimum. If the criterion is defined by

$$F = F(x_1, x_2, \ldots, x_n) \qquad \text{(II-93)}$$

then its gradient at a point $(x_1, x_2, \ldots, x_n)$ is defined by a vector

$$\text{grad } F = \left(\frac{\partial F}{\partial x_1}, \frac{\partial F}{\partial x_2}, \ldots, \frac{\partial F}{\partial x_n}\right) \tag{II-94}$$

The partial derivative $\partial f/\partial x_i$ is proportional to the cosine of the angle between the gradient vector and the i-axis of coordinates. Then

$$\frac{\dfrac{\partial F}{\partial x_i}}{\sqrt{\sum_{i=1}^{n}\left(\dfrac{\partial F}{\partial x_i}\right)^2}} = \cos(\text{grad } F\, x_i) \tag{II-95}$$

In addition to the direction of the gradient vector, a very important problem in the gradient methods is to decide on the step length in the direction of the gradient. The step size along grad F is to a considerable degree dependent on the nature of the performance surface. If the step is too short, lengthy calculations will result. If, on the other hand, the step is too long, the optimum may well be missed. The step size, Δx_i, should satisfy the condition which requires that all steps from the base point be in the direction of the gradient at the base point. For each variable x_i, the step size is found from the values of the partial derivatives at the base (starting) point:

$$\Delta x_i = \frac{K\dfrac{\partial F}{\partial x_i}}{\sqrt{\sum_{i=1}^{n}\left(\dfrac{\partial F}{\partial x_i}\right)^2}} \tag{II-96}$$

where K is a constant defining the step size and is the same in each of the i coordinate directions. It is only at the base point that the gradient is precisely orthogonal to the surface. If the step is too long in each of the i coordinate directions, the vector from the base point will not be orthogonal to the surface at the new point.

With a properly selected step size, the derivative at the next point will be substantially close to that at the base point.

For linear functions the direction of the gradient is independent of the position of the point on the surface for which it is calculated. If the surface has the form

$$F = c_1x_1 + c_2x_2 + c_3x_3$$

then

$$\partial F/\partial x_1 = c_1, \quad \partial F/\partial x_2 = c_2, \quad \partial F/\partial x_3 = c_3$$

and the gradient component in the ith coordinate direction will be

$$\frac{c_i}{\sqrt{c_1^2 + c_2^2 + c_3^2}} \tag{II-97}$$

For nonlinear functions, the direction of the gradient vector depends on the position of the point on the surface for which it is calculated.

Although there is a good deal of difference between the gradient methods, the procedure for seeking the optimum is in most cases about the same: (a) a base point is selected; (b) the direction of ascent (or descent) from the base point is ascertained; (c) the step size is found; (d) the next point of search is determined; (e) the value of the objective function at a given point is compared with that at the previous point; (f) the direction of movement is ascertained, etc. The procedure is repeated until the optimum is reached.

Method of steepest descent (ascent). As an example of a gradient method, we shall describe a procedure for minimizing functions of two variables:[11]

$$F = F(x_1, x_2) \tag{II-98}$$

subject to constraints

$$H_1(x_1, x_2) \leqslant 0, \quad H_2(x_1, x_2) \leqslant 0 \tag{II-99}$$

This principle can be generalized to any number of variables and any number of constraints.

Consider the x_1, x_2 plane (Fig. II-22). According to Eq. (II-98) each point on this plane corresponds to a particular value of F. The closed curves on this plane represent contours of constant F around the point M^* at which F has a minimum (maximum) value.

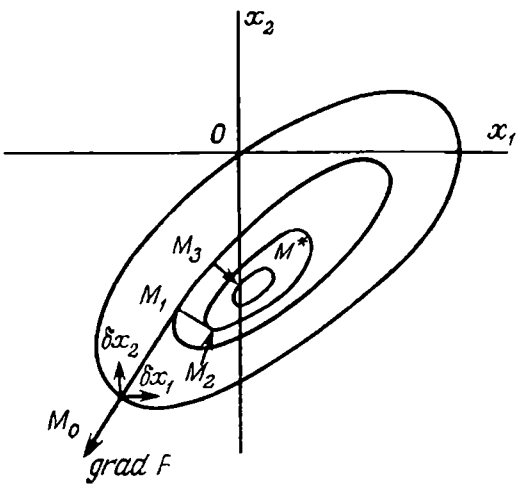


Fig. II-22. Search for a function minimum by the gradient method

The method of steepest descent operates as follows. To begin with, initial values (guesses) are provided for x_1 and x_2, such that they are at starting (base) point M_0, as well as an initial incremental change for these two parameters. The search process is started with a series of exploratory steps or moves. At first, x_1 is increased by a small amount, $\delta x_1 > 0$, while x_2 is held constant, and the change, δF_1, is measured in F, resulting from the manipulation of x_1. This change may be assumed to be proportional to the partial derivative

$$\partial F/\partial x_1 \approx \delta F_1/\delta x_1 = \text{const}\, \delta F_1 \tag{II-100}$$

(provided δx_1 is the same always). Then x_2 is increased by $\delta x_2 > 0$ while x_1 is held constant. The resultant change δF_2 in F is a measure of the partial derivative

$$\partial F/\partial x_2 \approx \delta F_2/\delta x_2 = \text{const}\, \delta F_2 \tag{II-101}$$

The partial derivatives given by (II-100) and (II-101) define a vector with coordinates $\partial F/\partial x_1$ and $\partial F/\partial x_2$, which is called the *gradient* of F, symbolized as

$$\text{grad}\, F = \{\partial F/\partial x_1, \quad \partial F/\partial x_2\} \tag{II-102}$$

The vector extends in the direction of the maximum increase in F at a given point (see Fig. II-22). The negative of the gradient is in the direction of steepest descent in F at that point.

After the gradient components defining a successful direction of search have been ascertained, exploratory steps or moves are discontinued, and pattern moves or steps are made in the negative direction of the gradient, the step size being in proportion to the magnitude of grad F. This condition is satisfied if the pattern step sizes, Δx_1 and $x\Delta_2$, are proportional to the partial derivatives obtained before:

$$\left.\begin{aligned}\Delta x_1 &= -\alpha \frac{\partial F}{\partial x_1} \\ \Delta x_2 &= -\alpha \frac{\partial F}{\partial x_2}\end{aligned}\right\} \qquad \text{(II-103)}$$

where α is a positive constant.

After each pattern move, the change ΔF in F is estimated. If the previous change has caused a decrease in F, the next move should be taken in the same direction, M_0M_1. If the change at M_1 has caused an increase in F (that is if $\Delta F > 0$), no pattern move is taken further, and exploratory moves are resumed. Then, again, grad F is estimated at the new point M_1, and pattern moves are resumed in the newly established direction of steepest descent, that is, along the line M_1M_2, etc. This is why the technique is called the *method of steepest descent* (in the case of minimization) or *ascent* (in the case of maximization).

When the quantity

$$\varepsilon = \left|\frac{\partial F}{\partial x_2}\right| + \left|\frac{\partial F}{\partial x_2}\right| \qquad \text{(II-104)}$$

drops to a small value, which is an indication that the system is in the vicinity of the minimum, a more conservative search technique is applied, called the *gradient method.* It differs from the method of steepest descent in that after grad F is determined, only one pattern move at a time is made, and exploratory moves are resumed at the new point. With this search technique, the minimum is located more accurately than with the method of steepest descent, although the latter secures the fastest approach to the minimum. If, during the search, the point M reaches the boundary of the feasible area and at least one of the quantities, M_1 or M_2, changes sign, the search procedure is modified so that the point M moves along the boundary.

The efficiency of the method of steepest descent depends on the scale of variables used and the nature of the response surface. The fastest approach to the optimum is attained in the case of a surface with spherical contours.

Among the demerits of the method of steepest descent are:

(1) Extrapolation is limited. In moving along the gradient, we are guided by the extrapolation of the derivatives of the objective function with respect to appropriate variables. However, the shape of the response surface may change, thereby necessitating a change in the direction of search. In other words, we cannot move on the surface for any considerable length of time (see Example II-11).

(2) A global optimum is difficult to find. The method is only applicable to finding local optima.

Method of steepest descent (ascent) with constraints. When some constraints are imposed on changes in the parameters of the objective function, the base point is chosen so that it will lie within the limits set by the constraints, and the search is conducted by the method of steepest descent (ascent) method. After the next point is calculated, a test is run to see if the constraints have been violated. If there is no violation, the search is resumed. If any constraint has been violated, the gradient is calculated so as to allow for the constraint (see below).

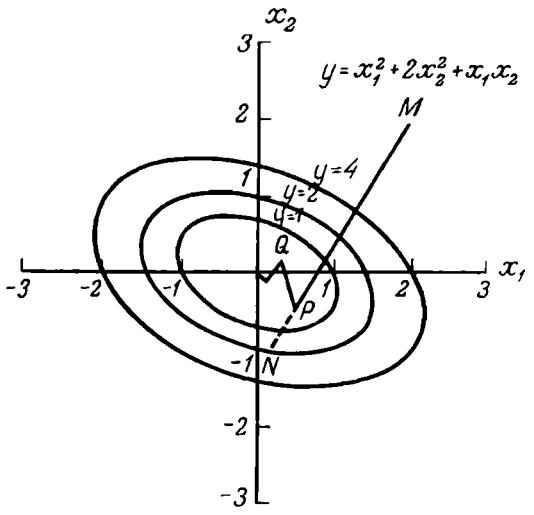


Fig. II-23. Search for an extremum by the steepest ascent method

As an alternative, a method[15] may be used in which the violation of a constraint causes the point to be returned to the constraint line. If more than one constraint have been imposed and a new constraint is violated at each new instant of time, the method requires that the points be moved to that new constraint. In this method, it is assumed that the optimum lies on a constraint.

In Rosenbrock's method,[16] the objective function is modified by the introduction of multipliers. Each time a variable violates a constraint, the multiplier is zero. That is, the objective function is multiplied by zero and is, therefore, equal to zero. If the variable remains within the feasible area, the multiplier is unity, and the objective function takes on its full value. However, when the variable drops to the limits prescribed by the "boundary region", the multiplier changes parabolically from 0 to 1 within the boundary region, and the objective function varies from 0 to its full value.

Example II-11.[17] Find the optimum by the method of steepest descent (ascent) for an objective function of the form

$$y = x_1^2+2x_2^2+x_1x_2$$

The starting point of the search has the coordinates $x_{10} = 2$ and $x_{20} = 2$ (point M in Fig. II-23)

Solution. The direction of the gradient is ascertained by finding the partial derivatives along the respective coordinate axes:

$$\partial y/\partial x_1 = 2x_1+x_2 \quad \partial y/\partial x_2 = 4x_2+x_1$$

At the starting point M, the partial derivatives respectively are:

$$\partial y/\partial x_1 = 2(2)+2 = 6 \quad \partial y/\partial x_2 = 4(2)+2 = 10$$

Both partial derivatives are positive, and so the objective function changes in the same direction as x_1 and x_2. If the function is to be minimized, x_1 and x_2 should be reduced until a minimum value is reached for y in the proportion:

$$\frac{\partial y}{\partial x_1} : \frac{\partial y}{\partial x_2} = 6 : 10 = 0.6$$

Let the first move cause x_2 to change by 0.5. Accordingly, x_1 will change by $0.6 \times 0.5 = 0.3$. Then we may write

$$x_{10} = 2 \quad x_{20} = 2 \quad y_0 = 16$$
$$x_1 = x_{10} - 0.3 = 2 - 0.3 = 1.7$$
$$x_2 = x_{20} - 0.5 = 2 - 0.5 = 1.5$$
$$y = (1.7)^2 + 2(1.5)^2 + (1.7)(1.5) = 9.94$$

On moving along the gradient, the objective function will progressively be descreasing, and we may write:

$$x_{12} = 1.4 \quad x_{22} = 1.0 \quad y_2 = 5.36$$
$$x_{13} = 1.1 \quad x_{23} = 0.5 \quad y_3 = 2.26$$
$$x_{14} = 0.8 \quad x_{24} = 0.0 \quad y_4 = 0.64$$
$$x_{15} = 0.5 \quad x_{25} = -0.5 \quad y_5 = 0.50$$
$$x_{16} = 0.2 \quad x_{26} = -1.0 \quad y_6 = 1.84$$

The line MN is the path of steepest descent from the starting point M. The point N represents x_{16} and y_6. Since we have passed the minimum of the function at y_5, we return to the point P corresponding to y_5, and determine the new direction of the gradient from the point P for $x_1 = 0.5$ and $x_2 = -0.5$:

$$\partial y/\partial x_1 = 2x_1 + x_2 = 1.0 - 0.5 = 0.5$$
$$\partial y/\partial x_2 = 4x_2 + x_1 = -2.0 + 0.5 = -1.5$$

From the above equalities it follows that $\partial y/\partial x_1$ is positive and $\partial y/\partial x_2$ is negative, and so the change in y is opposite to that in x_2. In other words, in order to minimize the objective function, x_2 should be increased. Since we are now in the vicinity of the optimum, the step size, Δx_2, should be reduced to 0.3. Since the ratio of Δx_1 to Δx_2 is 1-to-3 (which follows from the values of the partial derivatives), the respective change in x_1 will be 0.1.

Thus, the following new values will be obtained for the sixth step:

$$x_{16} = x_{15} - 0.1 = 0.5 - 0.1 = 0.4$$
$$x_{26} = x_{25} + 0.3 = -0.5 + 0.3 = -0.2$$
$$y_6 = (0.4)^2 + 2(-0.2)^2 + (0.4)(-0.2) = 0.16$$

On moving along the new gradient path, we find

$$x_{17} = 0.3 \quad x_{27} = 0.1 \quad y_7 = 0.14$$
$$x_{18} = 0.2 \quad x_{28} = 0.4 \quad y_8 = 0.44$$

The last point shows that we have passed the minimum again, because y_8 is greater than y_7. Now we reverse the direction again (point Q) as shown in Fig. II-23, and resume the calculations until we reach the optimum which, in our case, is the minimum value of y.

Example II-12.[17] Minimize the function $x_1^2+x_2$ subject to $x_1+x_2 \geqslant 4$. The starting point has the coordinates $x_1 = 3$ and $x_2 = 1$. Present the procedure graphically.

Solution. The objective function has the form

$$y = x_1^2+x_2$$

Find the partial derivatives of the objective function with respect to x_1 and x_2

$$\partial y/\partial x_1 = 2x_1 \qquad \partial y/\partial x_2 = 1$$

Thus, the ratio of a change in x_2 to that in x_1 is $1/2x_1$. At the starting point, we have $1/(2\times 3) = 1/6$.

Assuming that the change in x_1 is 0,5, the change in x_2 will be 0.08, and at the starting point we will then have

$$x_{12} = x_1-0.50 = 3.0-0.50 = 2.50$$
$$x_{22} = x_2-0.08 = 1.0-0.08 = 0.92$$

Recalling that the constraint imposed is $x_1+x_2 \geqslant 4$, for the found values of x_{12} and x_{22} we find

$$x_{12}+x_{22} = 2.50+0.92 = 3.42$$

which is a violation of the constraint.

Let the constraint be z, that is, $z = x_1+x_2$ and take the partial derivatives of the constraints:

$$\partial z/\partial x_1 = 1, \qquad \partial z/\partial x_2 = 1$$

Since the partial derivatives are equal, both x_1 and x_2 should be changed by the same amount. Let the incremental change be 0.35. Since the sum of x_1 and x_2 was too small, they should be increased so as to satisfy the inequality constraints. Thus,

$$x_{13} = x_{12}+0.35 = 2.50+0.35 = 2.85$$
$$x_{23} = x_{22}+0.35 = 0.92+0.35 = 1.27$$

The graph of the solution by the method of steepest descent is shown in Fig. II-24. The parabolas are contours of constant values of the objective function. The line MN represents the inequality constraint. The solution of the problem can only exist at x_1 and x_2 lying on, or to the right of, this line. The starting point is point *1*, and the next point is point *2*. As is seen, the con-

straint is violated, and point *3* moves back into the feasible area. Thus, the solution of the problem is: $x_1 = 0.50$ and $x_2 = 3.5$.

With this method, the movement from the unfeasible area is orthogonal to the constraint on the objective function.

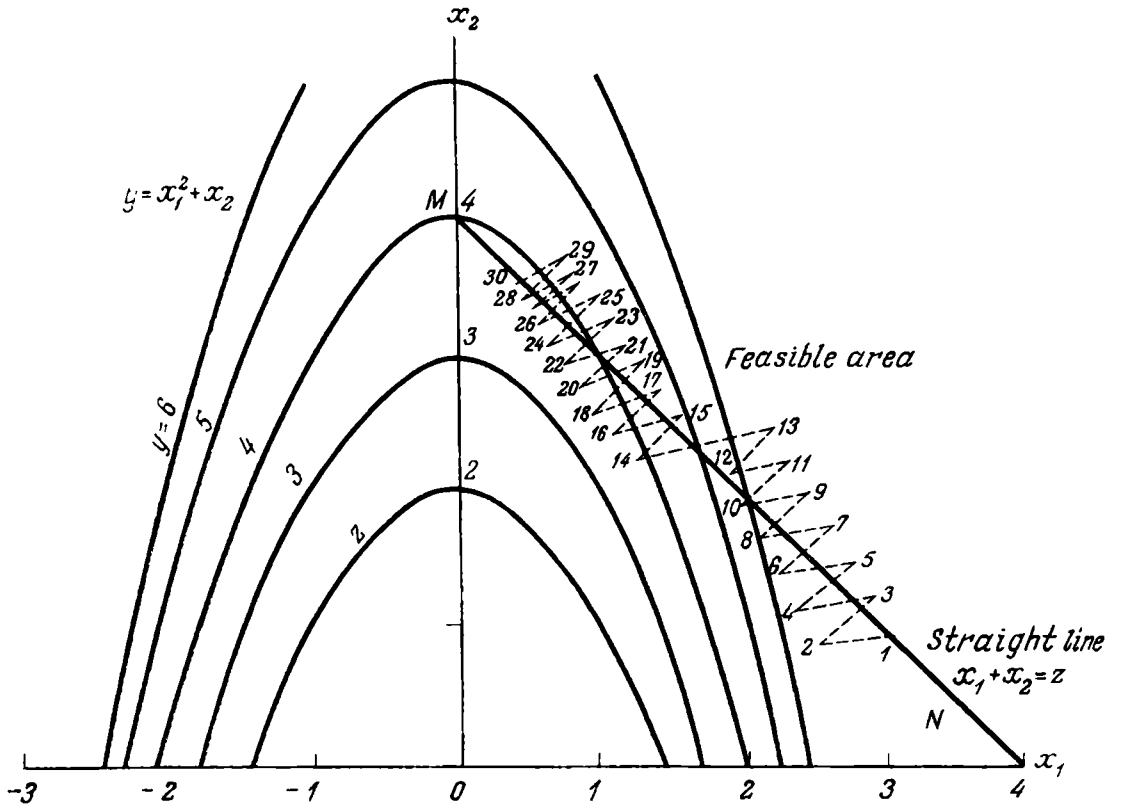


Fig. II-24. Search for an optimum under conditions of constraints

Two-derivative method. With this search method, the independent variable is continually incremented after each move by an amount equal to the negative ratio of the first to the second partial derivative. This is done until the optimum is reached.[18]

The method will be better understood from the following example. Let the function of one variable be a quadratic equation of the form

$$y = ax^2 + bx + c \qquad (a)$$

A plot of this function appears in Fig. II-25. It is seen that the function reaches an optimum at point $P(x_{opt}, y_{opt})$ after a number of consecutive moves from a starting point, $P(x_0, y_0)$. At the optimum point, $P(x_{opt}, y_{opt})$, the first derivative of equation (a) is equal to zero. The first derivative depicted on the plot of Fig. II-25 is expressed by

$$dy/dx = 2ax + b \qquad (b)$$

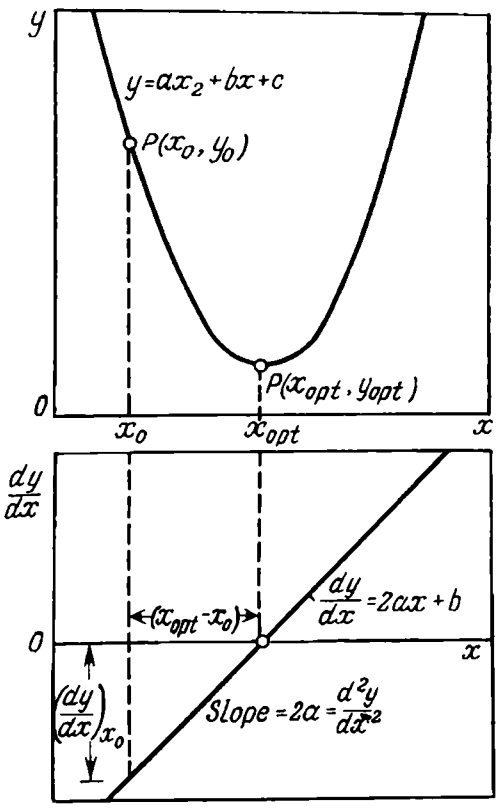


Fig. II-25. Search for an extremum by the two derivative method

Equation (*b*) describes a straight line with a slope of $2a$, numerically equal to the second derivative, d^2y/dx^2, of the original function. In our case, the second derivative is a constant, and no further calculations are necessary. An ideally optimal point could be reached immediately after the first step from point x_0 to point x_{opt} by adding to the starting value of x the amount $(x_{opt}-x_0)$, that is

$$x_{opt} = x_0+(x_{opt}-x_0) \qquad (c)$$

An analysis of the straight line described by Eq. (*b*) shows that $(x_{opt}-x_0)$ can be evaluated if one knows that the first derivative is equal to zero at point $P(x_{opt}, y_{opt})$, that is

$$(dy/dx)_{x_{opt}, y_{opt}} = 0 \qquad (d)$$

It is obvious that a slope of $2a$ may be expressed as follows

$$\frac{(dy/dx)_{x_{opt}, y_{opt}}-(dy/dx)_{x_0, y_0}}{x_{opt}-x_0} = 2a = d^2y/dx^2 \qquad (e)$$

Re-writing Eq. (*e*), we get

$$I_x = x_{opt}-x_0 = -\frac{(dy/dx)_{x_0, y_0}}{d^2y/dx^2} \qquad (f)$$

The above expression sums up the method of two derivatives. As is seen, the amount, I_x, by which the variable should be incremented at a given point is the negative ratio of the first derivative to the second derivative of the objective function.

Thus, I_x calculated for point $P(x_0, y_0)$ and incremented to x_0 leads precisely (in the case of a quadratic function) to x_{opt}. As an example, let the objective function be $y = x^2-10x$ for which the optimum values are $x_{opt} = 5$ and $y = -25$. Taking $x_0 = 1$ as a starting point and using Eq. (*f*), we find the step size to be $I_x = -(-8) \div -2 = 4$. Thus, the optimum value is $x = 1+4 = 5$. Any other value of the starting point would lead to the same optimum. After we have reached the point $P(x_{opt}, y_{opt})$, Eq. (*f*) yields an increment of zero for that point. This is an indication that the optimum has already been reached, and no further optimization is needed.

For a function of one independent variable, other than quadratic, the second derivative is found at point $P(x_0, y_0)$, because in the general case it

may vary with x, and the expression for the increment takes the form

$$I_{x,0} = -\frac{(dy/dx)_{x_0, y_0}}{(d^2y/dx^2)_{x_0, y_0}} \tag{II-105}$$

Let the objective function be $y = 300x - x^2$, subject to a constraint such that $x > 0$. The starting point is $x_0 = 5$ and $y_0 = 1.375$. After three moves, the method of two derivatives yields $x_3 = 10.003$ and $y_3 = 1999.997$, which are very close to optimal values, $x_{opt} = 10.0$ and $y_{opt} = 2000.0$

For a function of many variables, $\varphi = f(x, y, z, \ldots)$, the increment is found for each independent variable:

$$I_x = -\frac{\partial\varphi/\partial x}{\partial^2\varphi/\partial x^2} \tag{II-106}$$

$$I_y = -\frac{\partial\varphi/\partial y}{\partial^2\varphi/\partial y^2} \tag{II-107}$$

With the increments thus found, every move towards the optimum consists in adding the increment to the respective variable. On moving from point $P(x_0, y_0, \ldots)$ to point $P(x_1, y_1, \ldots)$ one gets a system of simultaneous equations

$$x_1 = x_0 + I_{x,0}$$

$$y_1 = y_0 + I_{y,0}$$

For a comparison, we shall find the optimum for the function $y = x_1^2 + 2x_2^2 + x_1x_2$ by the method of steepest descent (see p. 150). As before, the coordinates of the starting point are $x_{10} = 2$ and $x_{20} = 2$. The search for an optimum by the method of steepest descent and the method of two derivatives is compared in Table II-4.

Table II-4

Comparison of the Search for an Optimum by the Methods of Steepest Descent and Two Derivatives

Step No.	Steepest descent			Two-derivative		
	x_1	x_2	y	x_1	x_2	y
0	2.00	2.00	16.00	2.0000	2.0000	16.0000
1	1.70	1.50	9.94	1.0000	−0.5000	2.0000
2	1.40	1.00	5.36	0.2500	0.2500	0.2500
3	1.10	0.50	2.26	−0.1250	−0.625	0.0312
4	0.80	0.00	0.64	0.0312	0.0312	0.0039
5	0.50	−0.50	0.50	−0.0156	−0.0078	0.0004
6	0.20	−1.00	1.84	0.0039	0.0039	0.0000
6*	0.40	−0.20	0.16			
7	0.30	0.10	0.14			
8*	0.20	0.40	0.44			

* At these points, the direction of the search is changed.

The analytic solution yields the following values: $x_{1,opt} = 0.0$; $x_{2,opt} = 0.0$; and $y = 0.0$. As is seen from the above table, the method of two derivatives secures a faster approach to the optimum. The same applies to a comparison of the two-derivative and gradient methods.

(D) THE PRINCIPLE OF MAXIMALITY

This is a set of theorems from the theory of optimal processes, which establish the conditions necessary for developing an optimum control for a system.[19] It has been shown[20] that these conditions are sufficient. At the same time, it is assumed that the controlled system is described by a system of simultaneous ordinary differential equations of the form

$$dx_i/d\tau = f_i(x_1, \ldots, x_n, \quad u_1, \ldots, u_m) \quad i = 1, \ldots, n \qquad \text{(II-108)}$$

In Eqs. (II-108), x_i ($i = 1, \ldots, n$) represents a set of variables fully describing the state of the controlled system at any instant of time, while $u_1, \ldots, u_m$ are manipulated inputs.

In the theory of optimal processes, the set of variables, x, is usally called *phase coordinates*. Introducing the concept of a *phase space*, which is an n-dimensional space of x_i variables, the state of the controlled system at any instant of time will be represented by a point whose coordinates are $x_1(\tau)$, $\ldots, x_n(\tau)$. With time, the position of a point in a phase space will generally change. As this happens, the point traces out a trajectory, called the *phase trajectory of the system*. The parameters of this trajectory, that is, the manner in which the phase coordinates of the system change, are estimated by solving Eqs. (II-108). Thus, if the initial state of the system is specified such that

$$x_i|_{\tau=0} = x_{i0} \quad i = 1, \ldots, n \qquad \text{(II-109)}$$

its future behaviour can be estimated by solving Eqs. (II-108) under the initial conditions defined by Eq. (II-109).

The manipulated variables, u_k ($k = 1, \ldots, m$), which enter the equation describing the behaviour of the system along with the phase coordinates x_i, may generally be changed arbitrarily within certain limits defined by the relations

$$\alpha_k \leqslant u_k \leqslant \beta_k \quad k = 1, \ldots, m \qquad \text{(II-110)}$$

A change in the manipulated variables, u_k, brings about a change in the trajectory of the system in the phase space. If, now, the trajectory is associated with some quantitative efficiency (or performance) criterion, a problem of optimum control arises. The problem reduces to finding a strategy for the manipulation of the inputs u_k which will maximize (or minimize, as the case may be) the performance criterion. A few examples of this class of problems follow.

To begin with, let there be a well-stirred batch reactor in which an arbitrary exothermal reaction of the form $A \xrightarrow{k} B$ takes place. We let the reactor be controlled by manipulating the temperature of the cooling agent in the

cooling jacket of the reactor. The governing equations describing the behaviour of the reactor in our case have the form

$$\frac{dc_A}{d\tau} = -w_r(c_A, T) \tag{II-111}$$

$$\frac{dT}{d\tau} = \frac{q_r}{c_s} w_r(c_A, T) - \frac{K_V F}{V c_s}(T - T_m) \tag{II-112}$$

where c_A is the concentration of the feed reactant A in the reactor at time origin τ, T is the reactor temperature at that time, $w_r(c_A, T)$ is the reaction rate which may be an arbitrary function of the concentration c_A and the temperature T, q_r is the heat of reaction, c_s is the heat capacity of the stock, V is the stock volume, K_V is the heat transfer coefficient of the reactor, F is the surface area of heat transfer through the reactor wall, and T_m is the temperature of the heat-transfer medium (manipulated variable).

In this case, the objective of optimum control is to decide on the manner in which the temperature of the heat-transfer medium, T_m should be changed with time so as to minimize the time required for the reactant A to reach the desired fractional conversion. The initial conditions for Eqs. (II-111) and (II-112) are the prereaction characteristics of the raw materials loaded into the reactor

$$\left.\begin{aligned} c_A\big|_{\tau=0} &= c_{A0} \\ T\big|_{\tau=0} &= T_0 \end{aligned}\right\} \tag{II-113}$$

The above problem is a typical example of time minimization.

As a second example, we shall take up the optimization of the temperature profile in a plug-flow reactor for a reaction of any arbitrary complexity. Changes in the concentrations of the reactants along the reactor may then be described by the following equations

$$dc_i/dl = w_{ri}(c_1, \ldots, c_n, T) \quad i = 1, \ldots, n \tag{II-114}$$

where w_{ri} is the rate at which the ith component of the reactant mixture is formed per unit length (in the general case, it depends on the concentrations of all components and the temperature in a given section of the reactor).

For a plug-flow reactor, the problem may be stated in several ways. As before, we may formulate it as a problem of time optimization. Then, a strategy should be found for manipulating the temperature along the reactor so as to obtain the specified amount of products with a minimum reactor length.

As an alternative, a temperature profile may be sought which, for a reactor of a specified length L, would maximize or minimize some function of the reactant concentrations at the reactor exit, notably of the form

$$F = \sum \gamma_i c_i(L) \tag{II-115}$$

where γ specifies constants; some of them (but not all) may be set equal to zero.

The initial conditions for Eq. (II-114) are the reactant concentrations at the inlet to the reactor:

$$c_i \mid_{L=0} = c_{i0} \tag{II-116}$$

Naturally, if some of the reaction products are non-existent in the starting stock, the respective concentrations, c_{i0}, are set equal to zero.

Consider the application of the maximality principle to the optimization of the temperature profile for a plug-flow reactor, so as to maximize the function F specified by Eq. (II-115). The general procedure consists in that a set of auxiliary functions, ψ_i, are introduced, which are solutions for a set of simultaneous linear differential equations:

$$\frac{d\psi_i}{d\tau} = -\sum_{j=1}^{n} \frac{\partial w_{ri}^2}{\partial c_i} \psi_i \quad i = 1, \ldots, m \tag{II-117}$$

subject to the following boundary conditions:

$$\psi_i \mid_{l=L} = \psi_i \quad i = 1, \ldots, m \tag{II-118}$$

It should be noted that while the boundary conditions for Eq. (II-116) are specified at the reactor inlet, those for the auxiliary functions, ψ_i, are specified at the reactor exit.

Then, the function H is introduced, composed of functions w_{ri} and ψ_i, according to the expression

$$H = \sum_{i=1}^{n} \psi_i w_{ri} \tag{II-119}$$

Using the function H, Eqs. (II-114) and (II-117) may be re-cast to a more compact form

$$\frac{\partial c_i}{\partial \tau} = \frac{\partial H}{\partial \psi_i} \tag{II-120}$$

$$\frac{\partial \psi_i}{\partial \tau} = -\frac{\partial H}{\partial c_i} \tag{II-121}$$

It is proved* that if $T_{opt}(l)$ describes optimal changes in T with reactor length so that F is maximized, then the function H specified by Eq. (II-119) takes a maximum value at any reactor section. To find H, use is made of the functions w_{ri} into which $c_i(l)$ are substituted as solutions of Eqs. (II-114) obtained under the initial conditions specified by (II-116) and optimum changes in $T_{opt}(l)$; the functions ψ_i are found from the solution of Eqs. (II-117) under the boundary conditions specified by (II-118).

Thus, the optimization of the temperature profile reduces to manipulating the temperature at any reactor section so as to maximize the function H. Consider its application to consecutive first-order reactions of the type:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \tag{II-122}$$

* Since Eqs. (II-120) and (II-121) resemble the equations of motion used in analytical mechanics, the function H is often referred to as the *Hamiltonian*.

We seek a temperature profile which will maximize the concentration of the reaction product R at the exit of a plug-flow reactor of length L. The optimality (performance) criterion F has the form

$$F = C_R(L) \tag{II-123}$$

Assuming that the reaction rate constants depend on temperature according to the Arrhenius equation:

$$\left.\begin{aligned} k_1 &= k_{01} \exp(-E_1/RT) \\ k_2 &= k_{02} \exp(-E_2/RT) \end{aligned}\right\} \tag{II-124}$$

we may develop equations describing changes in concentrations with reactor length as follows

$$dc_A/dl = k_1 c_A \tag{II-125}$$

$$dc_R/dl = k_1 c_A - k_2 c_R \tag{II-126}$$

with the boundary conditions defined as

$$\left.\begin{aligned} c_A \,|_{l=0} &= c_{A0} \\ c_R \,|_{l=0} &= 0 \end{aligned}\right\} \tag{II-127}$$

Noting Eq. (II-117), simultaneous differential equations for the auxiliary functions ψ_i have the form

$$\frac{d\psi_1}{dl} = k_1\psi_1 - k_1\psi_2 \tag{II-128}$$

$$\frac{d\psi_2}{dl} = k_2\psi_2 \tag{II-129}$$

The boundary conditions for Eqs. (II-128) and (II-129) may be written as follows

$$\left.\begin{aligned} \psi_1 \,|_{l=L} &= 0 \\ \psi_2 \,|_{l=L} &= 1 \end{aligned}\right\} \tag{II-130}$$

According to Eq. (II-119), the function H may be written as follows:

$$H = -\psi_1 k_1 c_A + \psi_2(k_1 c_A - k_2 c_R) = k_1 c_A(\psi_2 - \psi_1) - k_2 c_R \psi_2 \tag{II-131}$$

According to the general procedure of the maximality principle, the temperature at any cross-section of the reactor should be chosen so as to maximize the function H at the specified values of c_A, c_R, ψ_1, and ψ_2.

The temperature which maximizes H can be found from the equation derived by setting the derivative $\partial H/\partial T$ equal to zero:

$$\frac{\partial H}{\partial T} = \frac{k_1 E_1}{RT^2} c_A(\psi_2 - \psi_1) - \frac{k_2 E_2}{RT^2} c_R \psi_2 = 0 \tag{II-132}$$

From Eq. (II-132), the optimum temperature at any cross-section of the reactor may be expressed as a function of c_A, c_R, ψ_1 and ψ_2:

$$T_{opt} = \frac{E_2 - E_1}{F \ln\left\{\dfrac{E_2}{E_1} \cdot \dfrac{k_{20}}{k_{10}} \cdot \dfrac{c_R \psi^2}{c_A(\psi_2 - \psi_1)}\right\}} \tag{II-133}$$

Substituting the expression for T_{opt} from Eq. (II-133) into Eqs. (II-125), (II-126), (II-128) and (II-129), we obtain a set of four simultaneous equations in four unknown functions, c_A, c_R, ψ_1, ψ_2, with the boundary conditions defined by (II-127) and (II-130). In fact, this is a boundary value problem with two-point boundary conditions. On solving the equations for $c_A(l)$, $c_R(l)$, $\psi_1(l)$ and $\psi_2(l)$ and substituting the solutions in Eq. (II-133), we can find the optimum temperature as a function of the distance from the reactor inlet, as has been formulated in the statement of the optimization problem.

In cases where the interest is in qualitative changes of temperature with reactor length, the solution of the above simultaneous differential equations need not be carried to completion. It will suffice to utilize some properties apparent from the general form of Eqs. (II-125), (II-126), (II-128) and (II-129).

From Eq. (II-129) and the boundary conditions (II-130) for the function ψ_2 it follows that this function increases positively over the entire range of changes in l. Obviously, changes in temperature with reactor length will follow changes in the fraction

$$\frac{E_2}{E_1} \cdot \frac{k_{20}}{k_{10}} \cdot \frac{c_R \psi_2}{c_A(\psi_2 - \psi_1)} \tag{II-134}$$

standing under the sign of logarithm in Eq. (II-133).

Consider the numerator and denominator of (II-134) separately. Using Eqs. (II-126) and (II-129), it is an easy matter to show that

$$(d/dl)(c_R \psi_2) = k_1 c_A \psi_2 \tag{II-135}$$

Similarly, for the derivative of the denominator:

$$(d/dl)[c_A(\psi_2 - \psi_1)] = k_2 c_A \psi_2 \tag{II-136}$$

The expression for the derivative of (II-134) thus is

$$\frac{d}{dl}\left(\frac{E_2}{E_1} \cdot \frac{k_{20}}{k_{10}} \cdot \frac{c_R \psi_2}{c_A(\psi_2 - \psi_1)}\right) = \frac{E_2}{E_1} \frac{c_A \psi_2}{[c_A(\psi_2 - \psi_1)]^2} [k_1 c_A(\psi_2 - \psi_1) - k_2 c_R \psi_2]$$

$$= \frac{E_2}{E_1} \cdot \frac{c_A \psi_2}{[c_A(\psi_2 - \psi_1)]^2} H \tag{II-137}$$

From the last expression it follows that the sign of the derivative is the same as that of the function H in Eq. (II-131).

We shall limit ourselves to a case where $E_1 < E_2$. It can be shown that under this assumption changes in H with temperature can be depicted by curve *1* in Fig. II-26. Curve *2* applies to a case where the function H as a function of temperature has no stationary point. In both cases, the optimum temperature which maximizes H corresponds to a positive value of H. Thus, the derivative (II-137) of Eq. (II-134) is positive and increases with increasing l. This implies that the optimum temperature defined by Eq. (II-133) decreases with increasing l. This is why an optimum temperature profile may have the shape shown in Fig. II-27.

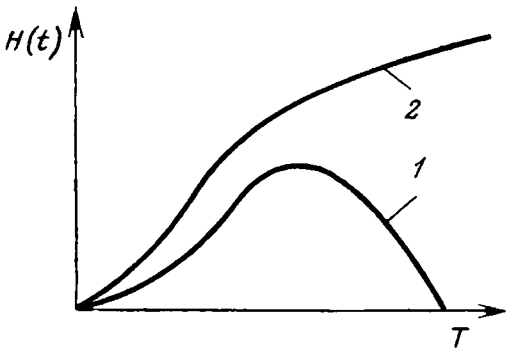


Fig. II-26. Hamiltionian, H, as a function of temperature

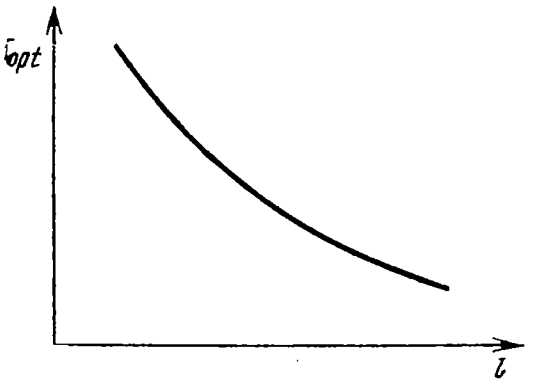


Fig. II-27. Optimum temperature profile

If the range of changes in temperature is bounded

$$T_{\min} \leqslant T \leqslant T_{\max} \tag{II-138}$$

cases may occur where a maximum temperature must be maintained at the head of the reactor ($T_{\max}$ in Fig. II-28). If, then, H is a monotonically rising function of temperature (see curve *2* in Fig. II-26), an optimum will be obtained with the temperature held at its maximum value over the entire length of the reactor (Fig. II-29).

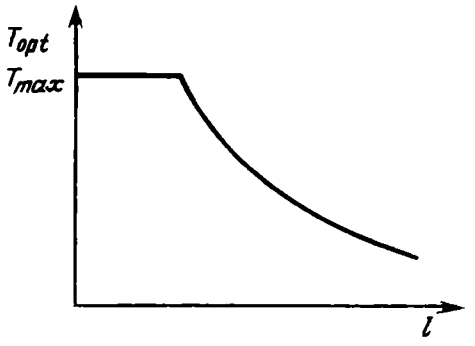


Fig. II-28. Maximum initial temperature in a reactor

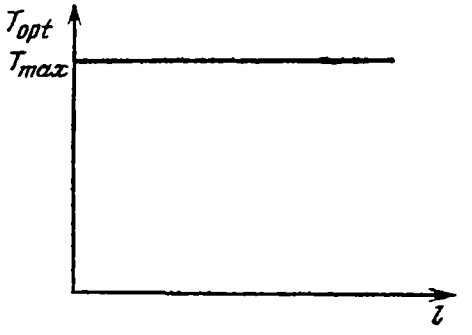


Fig. II-29. Optimum temperature conditions at a maximum temperature value along the reactor

As already noted, in the general case a precise quantitative calculation of an optimum temperature profile requires solution of Eqs. (II-125), (II-126), (II-128) and (II-129) under two-point boundary conditions (II-127) and (II-130). This involves a considerable amount of computational difficulties and usually calls for the use of digital computers.

A more detailed exposition of the optimization methods for chemical engineering will be found in [21] and [22].

(D) AUTOMATIC SEARCH FOR THE OPTIMUM

An automatic search for the optimum is usually conducted directly on the system or process in question.

The simplest automatic optimization systems in which an extremum is sought and maintained automatically without any additional constraints are called *extremal systems*. The device *A* (Fig. II-30) in such a system is called an *automatic optimizer*. A variety of automatic optimizers for a single variable have been described in the literature.

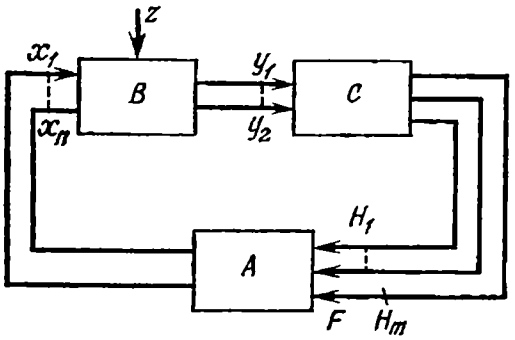


Fig. II-30. Automatic optimization of the process
A — optimizer; *B* — process; *C* — computer

Automatic optimization systems widely use computers as optimizers, simulators, performance computers, etc. In simple systems where no demand is made for the ultimate in accuracy, these may be inexpensive analog machines. In the more sophisticated systems, use is made of special-purpose multichannel optimizing computers of a hybrid type (that is, partly digital and partly analog). In some cases, optimizers are purely digital computers. In particularly elaborate cases where the processes are complicated and their performance has to be estimated as fully as practicable and to a high degree of accuracy, use is made of universal digital computers into which optimization programs are incorporated.

Automatic optimization grows more complicated as the number of manipulated (input) variables increases (Fig. II-30). For example, in a chemical reactor the process may be controlled by manipulating pressure, temperature and feed composition. Thus, in the general case (see Fig. II-30), the output variables $y_1, y_2, \ldots, y_n$ of the process and as a consequence, the quality criterion F are functions of several variables $x_1, x_2, \ldots, x_n$. The objective is to select values for x_i which will minimize (or maximize) F:

$$F = F(x_1, x_2, \ldots, x_n) = \text{extremum} \qquad (a)$$

Another complication is that in addition to the constraint stated above, there may be further constraints on the optimum. For example, in a distillation column it may be required to minimize the expenditure of steam per unit of product under conditions of further constraints.

Generally, some quantity, H_j ($j = 1, \ldots, m$), which is a function of manipulated (input) variables $x_1, x_2, \ldots, x_n$ of the process *B* (see Fig. II-30) should (be constrained to) remain within certain limits. This constraint may be defined by

$$H_j(x_1, x_2, \ldots, x_n) \leqslant 0 \qquad (b)$$

where $j = 1, \ldots, m$.

The values of H_j may be measured directly at the outlet from the process B or determined inferentially from the measurements of the system variables by a performance computer, C (see Fig. II-30). Then these values are fed together with the quantity being minimized, F, to the input of a multichannel automatic optimizer or optimizing computer (A in Fig. II-30). Then, the multichannel automatic optimizer seeks values for $x_1, x_2, \ldots, x_n$ which will minimize the performance function subject to the additional constraints.

In Fig. II-31, the task of an optimizer is illustrated by a geometric interpretation of a case involving two variables, x_1 and x_2. We lay off the values of the variables on Cartesian coordinates on a plane. Let $F = F(x_1, x_2)$ be laid off along a third coordinate axis perpendicular to the x_1, x_2 plane. The function $F(x_1, x_2)$ will be depicted on the z-plane in a three-dimensional space. The objective is to find such values, x_1^* and x_2^*, represented by point N^* on the x_1, x_2 plane, which will minimize F to a value equal to the height of point N^*. Initially, the values of x_1 and x_2 are represented by point M_0, and F is represented by the height of point N_0. Subsequent changes in x_1 and x_2 should be made so that point M with coordinates x_1, x_2, leaving, M_0, tends to move in the direction of M^*, and point N with coordinates (x_1, x_2, F) on leaving the position N_0 tends to move in the direction of N^*.

The motion and final position

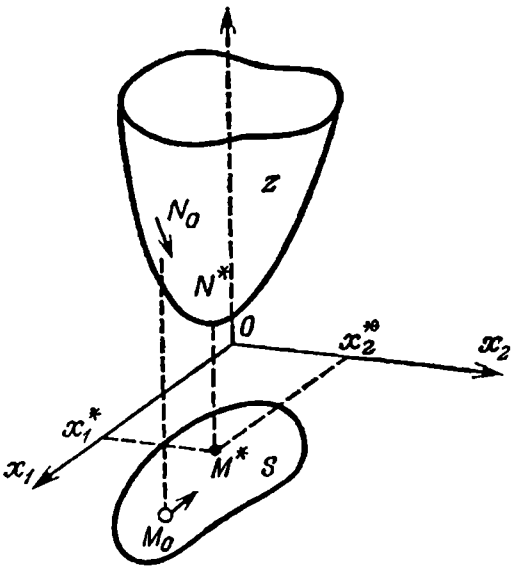


Fig. II-31. Explaining an automatic search for the optimum

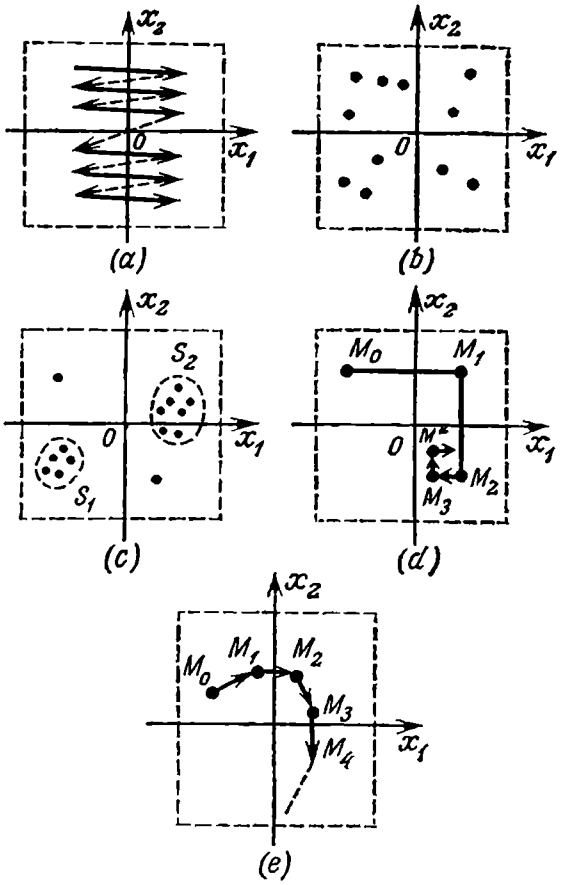


Fig. II-32. An automatic search for the optimum

(*a*) scanning; (*b*) a pure random search; (*c*) repetitive optimization; (*d*) local search; (*e*) Gauss-Seidel method

of point M should be such that condition (b) is satisfied always. This condition restricts the motion of point M to a feasible area, S, on the x_1, x_2 plane.

How should the search for x_1^* and x_2^* be conducted in order to minimize F? This question may be answered in a number of ways, some of which are described below.

Random search. In Fig. II-32, the feasible area for the variables is shown as a rectangle on the x_1, x_2 plane. In the general case, this area may be of any shape and even be multiply connected. The random search method consists in scanning points within the feasible area, following some pattern or at random, until a point for which F is a minimum is found. In Fig. II-32*a*, the feasible area is scanned in a predetermined pattern, say line by line. Another form is a purely random search in which points on the x_1, x_2 plane are sampled at random, but following some fixed distribution pattern (Fig. II-32*b*).

The random-search technique is unfortunately limited to relatively simple cases.

Search methods with repetitive analysis. In this group of methods, there is no predetermined search program. Every next step depends on the results of the preceding observations. Let, for example, the random search conducted at an earlier stage discover that lower values of F are concentrated in two sub-areas, S_1 and S_2 (shown by the dotted lines in Fig. II-32*c*). Then, one may suspect that the function F has two minima located in these subareas. On the basis of this "suspicion", the next search cycle is arranged to be confined solely or predominantly to these subareas. For example, if the initial search cycle has been one of random search, in the next cycle the probabilistic law which governs the formation of values for x_1 and x_2 is rearranged so that random points will occur within the subareas S_1 and S_2 more often.

Local search methods. This subgroup is of an especially important practical significance. With local search, the representative point M with coordinates (x_1, x_2) is caused to trace out a line, and these exploratory moves ascertain the direction in which pattern moves should be made so as to minimize the value of F.

In Fig. II-32*d*, for example, the representative point is moved from M along the x_1-axis in a direction which minimizes F. At the same time, x_2 = constant, and F solely depends on one variable, x_1. Let F be a minimum at point M. During the next cycle, x_2 is changed in a similar manner, and x_1 is held constant. Now, the representative point is moved from point M in parallel to the x_2-axis to, say, point M_2 where F takes on a new minimum. During the next cycle, x_1 is again changed, the representative point moves from M_2 to M_3, etc. As a result, the representative point approaches the position marked M^*, which defines the minimum of F.

The local search may be arranged so that the representative point will trace out a curve in the (x_1, x_2) plane (M_0, M_1, M_2, ... in Fig. II-32*e*). Such methods have already been described in connection with the method of steepest descent and the gradient method.

II-5. DEVELOPMENT OF MATHEMATICAL MODELS BY EXPERIMENT AND STATISTICS. STATISTICAL OPTIMIZATION

(A) BASIC CONCEPTS AND DEFINITIONS

In cases where we lack accurate information about a process or a process is complex to a point where a deterministic model is out of the question, resort is made to experimentation and statistics. In such cases, the process in question is treated as a black box, and its input-output relationships are studied through an experiment, which may be passive or active.

A *passive experiment* is a traditional variety in which a large number of observations are made, each variable being varied in turn. The concept of passive experiment also applies to the collection of statistical data in the normal operation of an industrial plant or process. The data thus collected are then reduced to develop a mathematical model by the classical methods of regression and correlation analysis.

An *active experiment* is carried out to a predetermined design (the *design of experiments*) and is usually arranged so as to cover all the governing process variables simultaneously, thereby permitting the experimentator to assess the strength of interaction between the variables and to cut down the amount of experimentation.

Regression and correlation analysis, when used judiciously, can give correct cues as to the relationships between process variables and optimum conditions. In both cases, the mathematical model is a response function which connects the optimization parameter which describes the outcome of an experiment to the variables which the experimentor manipulates in conducting the experiment:

$$y = \varphi(x_1, x_2, \ldots, x_k) \qquad \text{(II-139)}$$

The independent variables $x_1, x_2, \ldots, x_k$ are usually called *factors*, the coordinate space with coordinates $x_1, x_2, \ldots, x_k$ is called the *factorial space*, and a geometrical portrait of response functions in the factorial space is called a *response surface*.

This surface may be depicted as a contour diagram (Fig. II-33) relating, say, reaction yield (%) to temperature and concentration. In our case, the optimum yield is restricted to a small area on the response surface. If experiments were conducted and their outcomes analysed by conventional methods, that is, by varying only one variable at a time while holding the others constant,

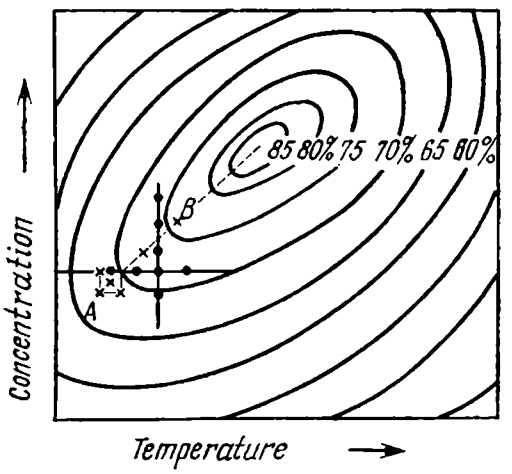


Fig. II-33. A response surface with an optimum

there wonld be a considerable probability of running into a false optimum (the dots in Fig. II-33). Apart from eliminating a false optimum, a properly designed experiment leads to the optimum region (the crosses in Fig. II-33) along the line *AB* at a faster rate.

With statistical methods, a mathematical model is a truncated Taylor series of some unknown relation, (II-139):

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{\substack{u,j=1 \\ u \neq j}}^{k} \beta_{uj} x_u x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \ldots \qquad \text{(II-140)}$$

where

$$\beta_j = \frac{\partial \varphi}{\partial x_j}\Big|_{\substack{\rightarrow \\ x=0}}; \quad \beta_{uj} = \frac{\partial^2 \varphi}{\partial x_u \partial x_j}\Big|_{\substack{\rightarrow \\ x=0}}; \quad \beta_{jj} = \frac{\partial^2 \varphi}{\partial x_j^2}\Big|_{\substack{\rightarrow \\ x=0}}$$

Since in a real process there are always uncontrolled and unobservable variables, changes in y are random in character. This is why in processing experimental data one uses *sample regression coefficients* b_0, b_j, b_{uj} and b_{jj} which are estimates of the theoretical coefficients β_0, β_j, β_{uj} and β_{jj}. The estimated regression equation developed on the basis of an experiment will then take the form

$$\hat{y} = b_0 + \sum_{j=1}^{k} b_j x_j + \sum_{u,j=1}^{k} b_{uj} x_u x_j + \sum_{j=1}^{k} b_{jj} x_j^2 + \ldots \qquad \text{(II-141)}$$

The coefficient b_0 is the *free term* of the regression equation, the coefficients b_j are *linear terms*, the coefficients b_{jj} are *quadratic terms*, and the coefficients b_{uj} are *interaction terms.*

The coefficients of Eq. (II-141) are estimated by the method of least squares from the condition

$$\Phi = \sum_{i=1}^{N} (y_i - \hat{y}_i)^2 = \min \qquad \text{(II-142)}$$

where N is the size of a sample out of the entire set of values of the parameters in question. The difference between the sample size N and the number of constraints, l, imposed on the sample, is the number of degrees of freedom, f, of the sample:

$$f = N - l \qquad \text{(II-143)}$$

In developing an equation of regression it is assumed that the number of constraints is equal to the number of coefficients sought.

The number of coefficients needed to be estimated in order to develop equations (polynomials) of different orders for 2 to 5 independent variables is given in Table II-5.

From Table II-5 it follows that the number of coefficients to be estimated rapidly increases with both the number of factors and the order of the equation.

The form of an equation of regression is found by trial-and-error.

Table II-5

Number of factors (independent variables)	Polynomial			
	first-order	second-order	third-order	fourth-order
	Number of coefficients			
2	3	6	10	15
3	4	10	20	35
4	5	15	35	70
5	6	21	56	126

(B) REGRESSION AND CORRELATION ANALYSIS

In establishing the average relationship between two variables associated with the same experiment, the form of the equation of regression can be deduced from the shape of an *empirical line of regression*. For this purpose, the entire range of changes in the independent variable, x, on the *correlation field* (Fig. II-34) is broken down into equal intervals Δx.

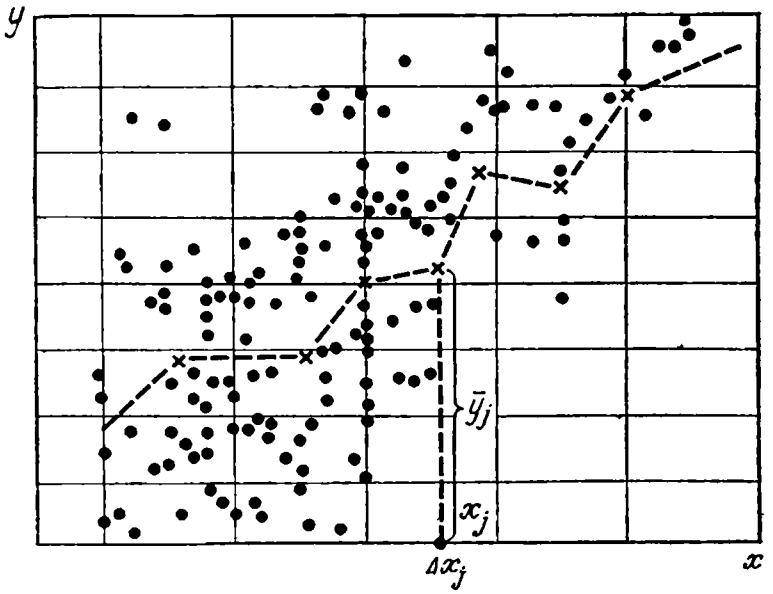


Fig. II-34. A correlation field

All points falling within a given interval Δx_j are referred to its centre, x_j. This is done by finding the sample mean, $\bar{y}_j$, for each sample interval:

$$\bar{y}_j = \frac{\sum_{i=1}^{n_j} x_{ji}}{n_j} \tag{II-144}$$

where n_j is the number of points within a given sample interval Δx_j.

$$\sum_{j=1}^{k} n_j = N \tag{II-145}$$

where k is the number of sample intervals and N is the sample size.

Then the points with coordinates $(x_j, \bar{y}_j)$ are connected by straight-line segments. The resultant broken line is the empirical line of regression. From the shape of the line of regression, one can select the form of the estimated equation of regression, $\hat{y} = f(x)$, that fits the line best.

The estimation of the parameters in an estimated equation of regression reduces to minimizing a function of many variables. If

$$\hat{y} = f(x, b_0, b_1, b_2, \ldots) \tag{II-146}$$

that is, if the function is differentiable and $b_0, b_1, b_2, \ldots$ should be selected so that

$$\Phi = \sum_{i=1}^{N} [y_i - f(x_i, b_0, b_1, b_2, \ldots)]^2 = \min \tag{II-147}$$

the necessary condition for minimizing $\Phi(b_0, b_1, b_2, \ldots)$ is to satisfy the equalities

$$\frac{\partial \Phi}{\partial b_0} = 0 \quad \frac{\partial \Phi}{\partial b_j} = 0 \quad \frac{\partial \Phi}{\partial b_2} = 0 \ldots \tag{II-148}$$

or

$$\left.\begin{aligned} \sum_{i=1}^{N} 2[y_i - f(x_i, b_0, b_1, b_2, \ldots)] \frac{\partial f(x_i)}{\partial b_0} = 0 \\ \sum_{i=1}^{N} 2[y_i - f(x_i, b_0, b_1, b_2, \ldots)] \frac{\partial f(x_i)}{\partial b_1} = 0 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right\} \tag{II-149}$$

After some manipulation, we obtain

$$\left.\begin{aligned} \sum_{i=1}^{N} y_i \frac{\partial f(x_i)}{\partial b_0} - \sum_{i=1}^{N} f(x_i, b_0, b_1, b_2, \ldots) \frac{\partial f(x_i)}{\partial b_0} = 0 \\ \sum_{i=1}^{N} y_i \frac{\partial f(x_i)}{\partial b_1} - \sum_{i=1}^{N} f(x_i, b_0, b_1, b_2) \frac{\partial f(x_i)}{\partial b_1} = 0 \end{aligned}\right\} \tag{II-150}$$

The set, (II-150), should have as many equations as there are unknown coefficients $b_0, b_1, b_2, \ldots$ in the estimated equation of regression. In mathematical statistics, it is called a *set (or system) of normal equations.*

At any values of $b_0, b_1, b_2, \ldots$, the quantity $\Phi \geqslant 0$. Therefore, it must have at least one minimum. In other words, if the system of normal equations has a unique solution, this solution is the minimum for Φ. The system of equations (II-150) cannot be solved in the general form, and so we must select a particular form for the function f.

Linear regression on one variable. We seek to estimate by the method of least squares the coefficients in a linear equation of regression of the form

$$\hat{y} = b_0 + b_1 x \tag{II-151}$$

from a sample of size N.

The set of normal equations for this case will be

$$\sum_{i=1}^{N} y_i - \sum_{i=1}^{N} (b_0 + b_1 x_i) = 0$$

$$\sum_{i=1}^{N} y_i x_i - \sum_{i=1}^{N} (b_0 + b_1 x_i) x_i = 0$$

or

$$\left.\begin{aligned} N b_0 + b_1 \sum_{i=1}^{N} x_i &= \sum_{i=1}^{N} y_i \\ b_0 \sum_{i=1}^{N} x_i + b_1 \sum_{i=1}^{N} x_i^2 &= \sum_{i=1}^{N} x_i y_i \end{aligned}\right\} \tag{II-152}$$

The coefficients b_0 and b_1 can best be estimated by means of the determinants

$$b_0 = \frac{\begin{vmatrix} \sum_{i=1}^{N} y_i & \sum_{i=1}^{N} x_i \\ \sum_{i=1}^{N} x_i y_i & \sum_{i=1}^{N} x_i^2 \end{vmatrix}}{\begin{vmatrix} N & \sum_{i=1}^{N} x_i \\ \sum_{i=1}^{N} x_i & \sum_{i=1}^{N} x_i^2 \end{vmatrix}} = \frac{\sum_{i=1}^{N} y_i \sum_{i=1}^{N} x_i^2 - \sum_{i=1}^{N} x_i \sum_{i=1}^{N} x_i y_i}{N \sum_{i=1}^{N} x_i^2 - \left(\sum_{i+1}^{N} x_i \right)^2} \tag{II-153}$$

$$b_1 = \frac{\begin{vmatrix} N & \sum_{i=1}^{N} y_i \\ \sum_{i=1}^{N} x_i & \sum_{i=1}^{N} x_i y_i \end{vmatrix}}{\begin{vmatrix} N & \sum_{i=1}^{N} x \\ \sum_{i=1}^{N} x_i & \sum_{i=1}^{N} x_i^2 \end{vmatrix}} = \frac{N \sum_{i=1}^{N} x_i y_i - \sum_{i=1}^{N} x_i \sum_{i=1}^{N} y_i}{N \sum_{i=1}^{N} x_i^2 - \left(\sum_{i=1}^{N} x_i \right)^2} \tag{II-154}$$

The coefficient b_0 can better be estimated once b_1 is known, from the first line in Eqs. (II-152):

$$b_0 = \bar{y} - b_1 \bar{x} \tag{II-155}$$

where $\bar{y}$ and $\bar{x}$ are the sample means of y and x.

Among other things, the last equation suggests the existence of a correlation between b_0 and b_1.

In order to estimate the strength of linear correlation, (II-151), a sample *coefficient of correlation*, r^*, is found

$$r^* = \frac{\sum_{i=1}^{N} (x_i - \bar{x})(y_i - \bar{y})}{(N-1)s_x s_y} \tag{II-156}$$

where s_x and s_y are the sample standard deviations.

From Eqs. (II-154) and (II-156), we have

$$r^* = \frac{b_1 s_x}{s_y} = b_1 \sqrt{\frac{N\sum_{i=1}^{N} x_i^2 - \left(\sum_{i=1}^{N} x_i\right)^2}{N\sum_{i=1}^{N} y_i^2 - \left(\sum_{i=1}^{N} y_i\right)^2}} \tag{II-157}$$

After an estimated regression equation is determined, it must be subjected to statistical analysis. This analysis consists in the following: all regression coefficients are tested for significance in comparison with the replication error, and the equation itself is tested for adequacy. This is *regression analysis.*

For regression analysis to be possible, the following conditions must be satisfied:

(1) The input variable x should be measured with a negligible error. Any error in the determination of x is due to the fact that the process has unobservable variables that are not included in the equation of regression.

(2) Measurements of the output variables $y_1, y_2, \ldots, y_N$ should be independent normally distributed random variables.

(3) In carrying out an experiment with a sample size N and with m replicate observations, the sample variances $s_1^2, s_2^2, \ldots, s_N^2$ must be the same, or homogeneous.

The variances are tested for homogeneity as follows:

(1) Find the mean of replicate observations:

$$\bar{y}_i = \frac{\sum_{u=1}^{m} y_{iu}}{m} \qquad i = 1, 2, \ldots, N \tag{II-158}$$

(2) Determine the sample variances:

$$s_i^2 = \frac{\sum_{u=1}^{m} (y_{iu} - \bar{y}_i)^2}{m-1} \qquad i = 1, 2, \ldots, N \tag{II-159}$$

(3) Find the sum of variances:

$$\sum_{i=1}^{N} s_i^2 \tag{II-160}$$

(4) Form the ratio

$$G_{\max} = \frac{s^2_{\max}}{\sum_{i=1}^{N} s_i^2} \tag{II-161}$$

where $s^2_{\max}$ is the maximum value of the sample variance.

If the variances are homogeneous, then

$$G_{\max} < G_p(N, m-1) \tag{II-162}$$

where $G_p(N, m-1)$ is the tabulated value of *Cochran's criterion* for a significance level p.[23]

If the sample variances are homogeneous, the error mean square is calculated

$$s_e^2 = \frac{\sum_{i=1}^{N} s_i^2}{N} \tag{II-163}$$

The error mean square has a number f of degrees of freedom, given by

$$f = N(m-1) \tag{II-164}$$

Knowledge of the error mean square is essential in testing the significance of the estimated coefficients of the regression equation, (II-151). This is done on the basis of the *Student t-test*:

$$t_j = \frac{|b_j|}{s_{b_j}} \tag{II-165}$$

where b_j is the jth estimated coefficient of the regression equation and s_{b_j} is the sample standard deviation of the jth coefficient.

If t_j exceeds the tabulated value of $t_p(f)$ for the selected significance level p and the number f of degrees of freedom, the estimated coefficient b_i is substantially non-zero; s_{b_j} is found by the error accumulation law[23]

$$s_{b_j} = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial b_j}{\partial y_i}\right)^2 s_i^2} \tag{II-166}$$

If $s_1^2 = s_2^2 = \ldots = s_N^2 = s_e^2$, then

$$s_{b_0} = \sqrt{\frac{s_e^2 \sum_{i=1}^{N} x_i^2}{N\sum x_i^2 - \left(\sum x_i\right)^2}} \tag{II-167}$$

$$s_{b_1} = \sqrt{\frac{s_e^2 N}{N\sum x_i^2 - \left(\sum x_i\right)^2}} \tag{II-168}$$

The nonsignificant estimated coefficients are dropped from the regression equation. The remaining estimated coefficients are recalculated, because they are intercorrelated. The equation is then tested for adequacy on the basis of *Fisher's variance ratio*:[23]

$$F = s_r^2/s_e^2 \tag{II-169}$$

where s_e^2 is the error mean square and s_r^2 is the residual mean square, defined by

$$s_r^2 = \frac{m \sum_{i=1}^{N} (\hat{y}_i - \bar{y}_i)^2}{N-l} \qquad \text{(II-170)}$$

where l is the number of coefficients in the regression equation.

If the ratio, (II-170), is smaller than the tabulated value of $F_p(f_1, f_2)$, the equation is an adequate fit.

In the absence of replicate observations and of an error mean square, the adequacy of the estimated regression equation can be tested by comparing s_r^2 and the estimated variance about the mean, s_y^2:

$$s_y^2 = \frac{\sum_{i=1}^{N} (y_i - \bar{y})^2}{N-1}$$

on the basis of Fisher's F-ratio test

$$F = s_y^2/s_r^2$$

In this case, the F-ratio is the factor by which the dispersion about the regression line is reduced relative to the dispersion about the mean. The greater the value of F in comparison with its tabulated value, $F_p(f_1, f_2)$, for the selected significance level p and the number of degrees of freedom, $f_1 = N-1$ and $f_2 = N-l$, the more efficient the estimated regression equation is.

Parabolic regression. If an estimated regression equation is a polynomial of some order, in the least squares method the coefficients of this polynomial are found by solving a system of linear equations. For example, it is desired to estimate the coefficients of a quadratic function, which is a second-order parabola defined by

$$\hat{y} = b_0 + b_1 x + b_{11} x^2 \qquad \text{(II-171)}$$

by the least squares method.

Then,

$$\partial f(x)/\partial b_0 = 1 \quad \partial f(x)/\partial b_1 = x \quad \partial f(x)/\partial b_{11} = x^2$$

and the system of normal equations has the form

$$\left.\begin{aligned} b_0 N + b_1 \sum x_i + b_{11} \sum x_i^2 &= \sum y_i \\ b_0 \sum x_i + b_1 \sum x_i^2 + b_{11} \sum x_i^3 &= \sum x_i y_i \\ b_0 \sum x_i^2 + b_1 \sum x_i^3 + b_{11} \sum x_i^4 &= \sum x_i^2 y_i \end{aligned}\right\} \qquad \text{(II-172)}$$

The coefficients for a parabola of any other order will be estimated by equations similar in structure.

Transcendental regression. With a small sample size, N, an increase in the order of the polynomial may lead to an increase in the residual mean square. The number of unestimated coefficients may be reduced through the use of transcendental regression. The calculation of transcendental regression

coefficients may prove a tedious task because one has to solve a system of nonlinear equations. The task may be simplified by using a transformation of variables. For example, exponential and fractional-power relations such as

$$\hat{y} = b_0 b_1^x, \quad \hat{y} = b_0 x^{b_1} \tag{II-173}$$

can be linearized by taking logarithms

$$\log_{10} \hat{y} = \log_{10} b_0 + x \log_{10} b_1$$

$$\log_{10} \hat{y} = \log_{10} b_0 + b_1 \log_{10} x$$

On setting

$$\log_{10} \hat{y} = \hat{z} \qquad \log_{10} b_0 = a$$

$$\log_{10} b_1 = a_1 \qquad \log_{10} x = t$$

we obtain linear equations in the new variables

$$\hat{z} = a_0 + a_1 x \qquad z = a_0 + b_1 t$$

The coefficients are estimated by the least squares method. Once a_0 and a_1 are found, one can estimate b_0 and b_1. It should be remembered, however, that the coefficients of regression equation (II-173) thus obtained are biassed estimators for the respective general coefficients.

Estimate of the strength of correlation. If we assume that a regression equation has been found with sufficient accuracy, the residual mean square will be only due to the error mean square that is

$$s_r^2 \approx s_e^2$$

The smaller the contribution of $s_r^2 \approx s_e^2$ to the overall estimated variance s_y^2, the stronger the correlation between y and x, because randomness in this correlation is reduced in proportion. Accordingly, the strength of correlation may be defined as

$$\xi = \frac{(N-l)s_r^2}{(N-1)s_y^2} \tag{II-174}$$

The value of ξ decreases with increasing strength of correlation. The quantity

$$\sqrt{1-\xi} = \theta \tag{II-175}$$

is termed the *index of correlation*. The greater the value of θ, the stronger the relationship between the two variables

$$0 \leqslant \theta \leqslant 1 \tag{II-176}$$

If $\theta = 1$, a functional relationship exists between the two variables. At $\theta = 0$, however, the variables y and x cannot be deemed independent. Without affecting the respective mean squares and variancies, the dependence between them may manifest itself in moments of a higher order. It is only in the case of normal distribution that a correlation index of zero may be

regarded as an indication that there is no functional relationship between the variables. Like the coefficient of correlation in linear regression, the index of correlation gives a measure of the degree of relationship between random variables. Analysis of correlation strength on the basis of θ constitutes *correlation analysis.*

With linear regression, the index of correlation is equal to the coefficient of correlation:

$$\theta = \sqrt{1 - \frac{N-2}{N-1} \cdot \frac{s_r^2}{s_y^2}} = r^*$$

Multiple correlation method.[24] If one is to analyse correlation between many variables, one uses a multiple regression equation of the form

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + \ldots + b_k x_k \qquad \text{(II-177)}$$

Instead of a regression line, one has to deal with a regression surface already at $k = 2$ and with a regression hypersurface at $k > 2$. In the general case, as already stated, this is a response surface.

In constructing a response surface, the numerical values of independent variables (factors) are laid off on the coordinate axes of a factor space. The statistical material used for the purpose is presented in tabular form like Table II-6.

Table II-6

Observation No.	x_1	x_2	x_3		x_k	y
1	x_{11}	x_{21}	x_{31}		x_{k1}	y_1
2	x_{12}	x_{22}	x_{32}		x_{k2}	y_2
3	x_{13}	x_{23}	x_{33}		x_{k3}	y_3
		.			.	
.	.	.	.		.	.
N	x_{1N}	x_{2N}	x_{3N}		x_{kN}	y_N

The first step is to transform the original data to a new scale. This is done by *normalizing* all random variables by the use of equations[25]

$$y_i^0 = \frac{y_i - \bar{y}}{s_y} \qquad x_{ji}^0 = \frac{x_{ji} - \bar{x}_j}{s_{x_j}} \qquad \begin{matrix} i = 1, 2, \ldots, N \\ j = 1, 2, \ldots, k \end{matrix} \qquad \text{(II-178)}$$

where y_i^0 and x_{ji}^0 are the normalized values of the respective factors, $\bar{y}$ and $\bar{x}$ are the sample means of the factors, s_y and s_{x_j} are the sample standard deviations of the factors defined as

$$s_y = \sqrt{\frac{\sum_{i=1}^{N} (y_i - \bar{y})^2}{N-1}} \qquad s_{x_j} = \sqrt{\frac{\sum_{i=1}^{N} (x_{ji} - \bar{x}_j)^2}{N-1}}$$

The statistical material after normalization is presented in Table II-7.

Table II-7

Observation No.	x_1^0	x_2^0	x_3^0	.....	y^0
1	x_{11}^0	x_{21}^0	x_{31}^0		y_1^0
2	x_{12}^0	x_{22}^0	x_{32}^0		y_2^0
3	x_{13}^0	x_{23}^0	x_{33}^0		y_3^0
.	.	.	.		.
.		.	.		.
.	.	.	.		.
N	x_{1N}^0	x_{2N}^0	x_{3N}^0		y_N^0

On the new scale we have

$$\begin{aligned} \bar{x}_j^0 &= 0 \quad \bar{y}_0 = 0 \\ s_{x_j^0} &= 1 \quad s_{y^0} = 1 \end{aligned} \tag{II-179}$$

Then the sample correlation coefficient is

$$\left.\begin{aligned} r^*_{y^0 x_j^0} &= \frac{1}{N-1}\sum_{i=1}^{N} y_i^0 x_{ji}^0 \\ r^*_{x_l^0 x_m^0} &= \frac{1}{N-1}\sum_{i=1}^{N} x_{li}^0 x_{mi}^0 \end{aligned}\right\} \tag{II-180}$$

$$l > m \quad l, m = 1, 2, \ldots, k$$

The sample correlation coefficient found from Eq. (II-180) is equal to the correlation coefficient for the variables taken on the natural scale, r^*_{yx}, (II-156).

The estimated regression equation for normalized variables has no free term and takes the form

$$\hat{y}^0 = a_1 x_1^0 + a_2 x_2^0 + \ldots + a_k x_k^0 \tag{II-181}$$

The coefficients of Eq. (II-181) are found from the condition

$$S = \sum_{i=1}^{N} (y_i^0 - \hat{y}_i^0)^2 = \text{minimum}$$

The conditions for the minimum of the function S are defined in the same manner as in the cases of a function of a single variable:

$$\partial S/\partial a_1 = 0 \quad \partial S/\partial a_2 = 0 \ldots \partial S/\partial a_k = 0 \tag{II-182}$$

and the set of simultaneous equations takes the form

$$a_1\sum_{i=1}^{N}(x_{1i}^0)^2+a_2\sum_{i=1}^{N}x_{1i}^0x_{2i}^0+\ \ldots\ +a_k\sum_{i=1}^{N}x_{1i}^0x_{ki}^0=\sum_{i=1}^{N}x_{1i}^0y_i^0$$

$$a_1\sum_{i=1}^{N}x_{2i}^0x_{1i}^0+a_2\sum_{i=1}^{N}(x_{2i}^0)^{0.2}+\ \ldots\ +a_k\sum_{i=1}^{N}x_{2i}^0x_{ki}^0=\sum_{i=1}^{N}x_{2i}^0y_i^0$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$a_1\sum_{i=1}^{N}x_{ki}^0x_{1i}^0+a_2\sum_{i=1}^{N}x_{ki}^0x_{2i}^0+\ \ldots\ +a_k\sum_{i=1}^{N}(x_{ki})^2=\sum_{i=1}^{N}x_{ki}^0y_i^0 \qquad \text{(II-183)}$$

Multiplying the left- and right-hand sides of the equation by $1/(N-1)$, we get a sample correlation coefficient, r^*, according to Eq. (II-183), for each coefficient a_j. Noting that

$$\frac{1}{N-1}\sum_{i=1}^{N}(x_{ji}^0)^2=s_{x_j^0}^2=1$$

we have a system of normal equations of the form

$$a_1+a_2r_{x_1x_2}^*+a_3r_{x_1x_3}^*+\ \ldots\ +a_kr_{x_1x_k}^*=r_{yx_1}^*$$

$$a_1r_{x_2x_1}^*+a_2+a_3r_{x_2x_3}^*+\ \ldots\ +a_kr_{x_2x_k}^*=r_{yx_2}^*$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$a_1r_{x_kx_1}^*+a_2r_{x_kx_2}^*+a_{3x_kx_3}^*+\ \ldots\ +a_k\ =r_{yx_k}^* \qquad \text{(II-184)}$$

It should be remembered that $r_{x_lx_m}^*=r_{x_mx_l}^*$. The correlation coefficients can readily be found by multiplying together the respective columns in Table II-7. For multivariable processes, Eq. (II-184) has a very high order, and it can be solved only on a computer.

On solving Eq. (II-184), one finds the *coefficient of multiple correlation*, R:

$$R=\sqrt{a_1r_{yx_1}^*+a_2r_{yx_2}^*+\ \ldots\ +a_kr_{yx_k}^*} \qquad \text{(II-185)}$$

The coefficient of multiple correlation is a measure of the strength of correlation in the case of multiple regression:

$$0\leqslant R\leqslant 1 \qquad \text{(II-186)}$$

With samples of small size, the value of R must be corrected for the systematic error. The fewer the degrees of freedom, $f=N-l$, the more the degree of correlation given by the multiple correlation coefficient is overestimated. The correction formula[25] is defined as

$$R'=\sqrt{1-(1-R^2)\frac{N-1}{N-l}} \qquad \text{(II-187)}$$

where R' is the corrected multiple correlation coefficient, l is the number of coefficients in the regression equation. For Eq. (II-177), $l = k+1$.

Before Eq. (II-181) can be used for practical purposes, one should change back to the natural scale, using the equations

$$\begin{aligned} b_j &= a_j \frac{s_y}{s_{x_j}} \quad j = 1, 2, \ldots, k \\ & \qquad j \neq 0 \\ b_0 &= \bar{y} - \sum_{j=1}^{k} b_j \bar{x}_j \end{aligned} \tag{II-188}$$

With replicate observations, one can calculate the error mean square and analyse the estimated regression equation statistically.

Regression analysis in matrix form.[26] This form of regression analysis is readily adaptable to computer solution. The first step is to estimate the coefficients of the regression equation by the least squares procedure on the basis of Table II-7:

$$\hat{y} = b_0 x_0 + b_1 x_1 + b_2 x_2 + \ldots + b_k x_k \tag{II-189}$$

where x_0 is a dummy variable equal to unity.

Now the original statistical material is presented in matrix form. The matrix

$$X = \begin{bmatrix} x_{01} & x_{11}, & \ldots, & x_{k1} \\ x_{02} & x_{12}, & \ldots, & x_{k2} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ x_{0N} & x_{1N}, & \ldots, & x_{kN} \end{bmatrix} \tag{II-190}$$

will be called a *matrix of independent variables*, and the column vector

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_N \end{bmatrix} \tag{II-191}$$

will be called the *observation vector*. We also introduce a coefficient matrix of the form

$$B = \begin{bmatrix} b_0 \\ b_1 \\ \vdots \\ b_k \end{bmatrix}$$

and the transpose of matrix X

$$X^* = \begin{bmatrix} x_{01} & x_{02}, \ldots, x_{0N} \\ x_{11} & x_{12}, \ldots, x_{11N} \\ \ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots \\ x_{k1} & x_{k2}, \ldots, x_{kN} \end{bmatrix} \tag{II-192}$$

The set of normal equations for estimating $b_0, b_1, \ldots, b_k$ has the form

$$\begin{aligned} &b_0 \sum x_{0i}^2 + b_1 \sum x_{0i}x_{1i} + \ldots + b_k \sum x_{0i}x_{ki} = \sum x_{0i}y_i \\ &b_0 \sum x_{1i}x_{0i} + b_1 \sum x_{1i}^2 + \ldots + b_k \sum x_{1i}x_{ki} = \sum x_{1i}y_i \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ &b_0 \sum x_{ki}x_{0i} + b_1 \sum x_{ki}x_{1i} + \ldots + b_k \sum x_{ki}^2 = \sum x_{ki}y_i \end{aligned} \tag{II-193}$$

in matrix form, they reduce to

$$X^*XB = X^*Y \tag{II-194}$$

For multiplying matrix X^* by matrix X gives

$$X^*X = \begin{bmatrix} \sum x_{0i}^2 & \sum x_{0i}x_{1i}, \ldots, \sum x_{0i}x_{ki} \\ \sum x_{1i}x_{0i} & \sum x_{1i}^2, \ldots, \sum x_{1i}x_{ki} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \sum x_{ki}x_{0i} & \sum x_{ki}x_{1i}, \ldots, \sum x_{ki}^2 \end{bmatrix} \tag{II-195}$$

Multiplying matrix X^*X by the B column vector gives a column vector

$$X^*XB = \begin{bmatrix} b_0 \sum x_{0i}^2 + b_1 \sum x_{0i}x_{1i} + \ldots + b_k \sum x_{0i}x_{ki} \\ b_0 \sum x_{1i}x_{0i} + b_1 \sum x_{1i}^2 + \ldots + b_k \sum x_{1i}x_{ki} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ b_0 \sum x_{ki}x_{0i} + b_1 \sum x_{ki}x_{1i} + \ldots + b_k \sum x_{ki}^2 \end{bmatrix} \tag{II-196}$$

Multiplying matrix X^* by the observation vector, Y, we obtain

$$X^*Y = \begin{bmatrix} \sum x_{0i}y_i \\ \sum x_{1i}y_i \\ \ldots\ldots \\ \ldots\ldots \\ \sum x_{ki}y_i \end{bmatrix} \tag{II-197}$$

From Eq. (II-194), the column vector, B, of coefficients is defined as

$$B = (X^*X)^{-1}X^*Y \tag{II-198}$$

where $(X^*X)^{-1}$ is an inverse of matrix (X^*X):

$$(X^*X)^{-1} = \begin{bmatrix} c_{00}, c_{01}, \ldots, c_{0k} \\ c_{10}, c_{11}, \ldots, c_{1k} \\ \ldots\ldots\ldots\ldots \\ c_{k0}, d_{k1}, \ldots, c_{kk} \end{bmatrix} \tag{II-199}$$

The elements of the inverse matrix are defined by the relation

$$c_{jk} = \frac{\left(\sum_{i=1}^{N} x_{ki}x_{ji}\right)}{\Delta} \tag{II-200}$$

where Δ is the determinant of matrix X^*X, $(\sum x_{ki}x_{ji})'$ is the cofactor of the element $(\sum x_{ki}x_{ji})$ in matrix X^*X.

For an inverse matrix to exist, matrix X^*X must be non-degenerate. Therefore, in using this method of calculation, it is important that the variables $x_1, x_2, \ldots, x_k$ be linearly independent. Then the elements of one column in the matrix of independent variables will not be a linear combination of the respective elements in other columns.

It is necessary to calculate the sample correlation coefficients for the factors in advance. If two factors are strongly correlated, one of them should be dropped from examination.

To find the residual mean square, one should evaluate the $\hat{Y}$ column vector

$$\hat{Y} = \begin{bmatrix} \hat{y}_1 \\ \hat{y}_2 \\ \vdots \\ \hat{y}_N \end{bmatrix} = XB \tag{II-201}$$

The numerator of the residual mean square is found by multiplying the matrices together:

$$[Y-\hat{Y}]^*[Y-\hat{Y}] = \sum_{i=1}^{N} (y_i-\hat{y}_i)^2 \tag{II-202}$$

Let β designate the column vector of true regression coefficients and let the expected value of B be $M(B) = \beta$. Then

$$M[(B-\beta)(B-\beta)^*] = \begin{bmatrix} \sigma^2_{b_0} & \text{cov}_{b_0b_1}, \ldots, \text{cov}_{b_0b_k} \\ \text{cov}_{b_1b_0} & \sigma^2_{b_1}, \ldots, \text{cov}_{b_1b_k} \\ \ldots\ldots\ldots\ldots\ldots\ldots & \\ \ldots\ldots\ldots\ldots\ldots\ldots & \\ \text{cov}_{b_kb_0} & \text{cov}_{b_kb_1}, \ldots, \sigma^2_{b_k} \end{bmatrix} \tag{II-203}$$

where σ^2_{bj} is the variance of b_j, $\text{cov}_{b_jb_k}$ is the covariance, or the correlation moment between b_j and b_k.

Thus, the diagonal terms of the matrix are the coefficient variances required for significance testing, while the nondiagonal terms are the covariances

of the respective regression estimators determining the statistical relationship between the coefficients.

Let the matrix $M[(B-\beta)(B-\beta)^*]$ be expressed in terms of observations, noting that $B = (X^*X)^{-1}X^*Y$.

We introduce a column vector

$$\overset{0}{Y} = Y - M(Y) = \begin{bmatrix} y_1 - m(y_1) \\ y_2 - m(y_2) \\ \vdots \\ y_N - m(y_N) \end{bmatrix}$$

This is a random normal vector with independent elements having a variance of σ_y^2. Hence:

$$M[(B-\beta)(B-\beta)^*] = M\left\{(X^*X)^{-1}X^*\overset{0}{Y}\left[(X^*X)^{-1}X^*\overset{0}{Y}\right]^*\right\}$$

The coefficient matrix of normal equations is symmetrical, and so

$$[(X^*X)^{-1}]^* = (X^*X)^{-1}$$

Putting $\sigma_{y_1}^2 = \sigma_{y_2}^2 = \ldots = \sigma_{y_N}^2 = \sigma_y^2$ and recalling that errors are statistically independent, we get

$$M\left(\overset{0}{Y}\overset{0}{Y}^*\right) = \begin{bmatrix} \sigma_{y_1}^2 & & & 0 \\ & \sigma_{y_2}^2 & & \\ & & \ddots & \\ 0 & & & \sigma_{y_N}^2 \end{bmatrix} = E\sigma_y^2 \qquad \text{(II-204)}$$

Thus, we have

$$M[(B-\beta)(B-\beta)^*] = (X^*X)^{-1}\sigma_y^2 \qquad \text{(II-205)}$$

whence

$$\sigma_{b_j}^2 = c_{jj}\sigma_y^2 \quad \text{cov}_{b_j b_k} = c_{jk}\sigma^2 \qquad \text{(II-206)}$$

The matrix $(X^*X)^{-1}$ is called an *error matrix*, or a *correlation matrix*.

Since the correlation matrix is non-diagonal and, as a consequence, all regression coefficients are interrelated, each coefficient cannot be tested for significance separately. Therefore the relation

$$t_j = \frac{|b_j|}{s_y\sqrt{c_{jj}}} \qquad \text{(II-207)}$$

can only be looked upon as a means for ranking the factors. A procedure has been proposed[27] for consecutively eliminating insignificant factors: a factor for which t_j is the least is dropped, and the calculation is repeated, as long as the residual mean square descreases. This improves the interpolating properties of the regression equation, but the resultant coefficients are biassed estimates.

With a large number of factors, the calculation of multiple regression calls for the use of a digital computer.

Development of multiple regression equations by Brandon's method.[28] In this method, the estimated regression equation is given the form

$$\hat{y} = af_1(x_1)f_2(x_2) \ldots f_j(x_j) \ldots f_k(x_k) \qquad \text{(II-208)}$$

where $f_j(x_j)$ is any function of x_j.

The arrangement of the factors $x_1, x_2, \ldots, x_k$ in Eq. (II-208) has a direct bearing on the accuracy in the reduction of observations: the greater the effect that x_j has on y, the smaller the j-index should be. The form of the function f_j is chosen on the basis of graphical construction. To begin with, a correlation field and an empirical regression line, $y-x_1$, are plotted on the basis of samples of quantities $y, x_1, x_2, \ldots, x_k$. Thus, one finds that

$$\hat{y}_{x_1} = f_1(x_1)$$

and, using the least squares procedure, estimates the coefficients of this regression equation. Now a new sample is built up

$$y_1 = \frac{y}{f_1(x_1)} \qquad \text{(II-209)}$$

This quantity is no longer dependent on x_1, and is solely determined by the parameters $x_2, x_3, \ldots, x_k$. Therefore, one may write

$$\hat{y}_1 = af_2(x_2)f_3(x_3), \ldots, f_k(x_k) \qquad \text{(II-210)}$$

Using new samples of y_1 and x_2, another correlation field and another empirical regression line depicting the dependence of y_1 on x_2 are constructed such that

$$\hat{y}_{x_2} = f_2(x_2)$$

The coefficients are again estimated, and a sample of the new quantity is built up

$$y_2 = \frac{y_1}{f_2(x_2)} = \frac{y}{f_1(x_1)f_2(x_2)} \qquad \text{(II-211)}$$

This quantity is independent of two factors, x_1 and x_2, and can be found from the following regression equation:

$$\hat{y}_2 = af_3(x_3), \ldots, f_k(x_k) \qquad \text{(II-212)}$$

This procedure is iterated until the sample of y_k is obtained

$$y_k = \frac{y_{k-1}}{f(x_k)} = \frac{y}{f_1(x_1)f_2(x_2), \ldots, f_k(x_k)} \qquad \text{(II-213)}$$

This quantity is independent of all factors, $x_1, \ldots, x_k$ and is defined by the coefficient of the original equation, Eq. (II-208)

$$\hat{y}_k = a = \frac{1}{N}\sum_{i=1}^{N} y_{ki}$$

where N is the sample size.

(C) STRATEGIES FOR EFFICIENT EXPERIMENTATION

One of the most important aspects of empirical model building is the design of experiments, that is, the selection of a strategy to obtain an adequate model with a minimum of experimentation.

Factorial (2^k) experimental designs. In a factorial experiment, a certain number of fixed values, or levels, are assigned to each factor, or each experimental variable which is deliberately varied from experiment to experiment.[26] If all possible combinations of the factors are used, the experiment is called a *full factorial design.* If k variables are to be controlled at two levels each, the experiment is termed a *full two-level factorial experiment* for k factors, or *2^k design* in brief.

The factor levels are in effect the boundaries of the area to be searched for a given process variable. Let one be interested in the effect of three factors on the product yield y, namely temperature T in the range 100 -200°C, pressure P in the range 20-60 atm, and residence time τ in the range 10 to 30 min. If the upper level for temperature is $z_1^{\max} = 200°C$, the lower level is $z_1^{\min} = 100°C$, then $z_1^0 = 150°C$, $\Delta z_1 = 50°C$, defined by

$$z_1^0 = \frac{z_1^{\max} + z_1^{\min}}{2}$$

$$\Delta z_1 = \frac{z_1^{\max} - z_1^{\min}}{2}$$

Generally, for any factor z_j, we have

$$z_j^0 = \frac{z_j^{\max} + z_j^{\min}}{2} \qquad j = 1, 2, \ldots, k \tag{II-214}$$

$$\Delta z_j = \frac{z_j^{\max} - z_j^{\min}}{2} \tag{II-215}$$

The point with coordinates $(z_1^0, z_2^0, \ldots, z_k^0)$ is called the *centre point of the design*, or the *basic level*, Δz_j is the *change interval* or *unit* on the z_j -axis. It is usual to pass from the $z_1, z_2, \ldots, z_k$ coordinates to a new dimensionless system of coordinates, $x_1, x_2, \ldots, x_k$, by the coding equation

$$x_j = \frac{z_j - z_j^0}{\Delta z_j} \qquad j = 1, 2, \ldots, k \tag{II-216}$$

In the dimensionless coordinate system, the upper level is $+1$, the lower level is -1, the coordinates of the centre point of the design are zero and coincide with the origin of coordinates. In our problem, $k = 3$. The number of all possible combinations, N, of three factors each controlled at two levels is $N = 2^k = 2^3 = 8$. The experimental design (the design matrix) may be reduced to a table such as Table II-8. The values of y, or the yield, obtained by carrying out the experimental design, are given in the last column of the table.

Geometrically, the coded design of Table II-8 may be interpreted as a cube (Fig. II-35), in which the eight corners represent the eight experimental points.

Table II-8

Two-Level Three-Factor (2^3) Design Matrix

Factors on natural scale				Factors on dimensionless scale			Yield
Observation No.	z_1	z_2	z_3	x_1	x_2	x_3	y
1	100	20	10	−1	−1	−1	2
2	200	20	10	+1	−1	−1	6
3	100	60	10	−1	+1	−1	4
4	200	60	10	+1	+1	−1	8
5	100	20	30	−1	−1	+1	10
6	200	20	30	+1	−1	+1	18
7	100	60	30	+1	+1	+1	8
8	200	60	30	+1	+1	+1	12

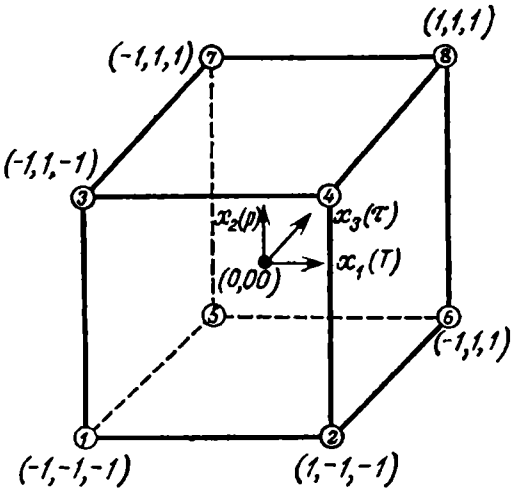


Fig. II-35. Geometric interpretation of a coded design

Table II-9

Design Matrix with a Dummy Variable

N	x_0	x_1	x_2	x_3	y
1	+1	−1	−1	−1	y_1
2	+1	+1	−1	−1	y_2
3	+1	−1	+1	−1	y_3
4	+1	+1	+1	−1	y_4
5	+1	−1	−1	+1	y_5
6	+1	+1	−1	+1	y_6
7	+1	−1	+1	+1	y_7
8	+1	+1	+1	+1	y_8

Let us write the 2^3 design matrix and the experimental results by introducing a column for a *dummy variable*, $x_0 = 1$.

The design matrix presented in Table II-9 has the following properties:

$$\sum_{i=1}^{N} x_{ui} \cdot x_{ji} = 0 \quad u \neq j \quad u, j = 0, 1, \ldots, k \tag{II-217}$$

$$\sum_{i=1}^{N} x_{ji} = 0 \quad j = 1, 2, \ldots, k \quad j \neq 0 \tag{II-218}$$

$$\sum_{i=1}^{N} x_{ji}^2 = N \quad j = 0, 1, \ldots, k \tag{II-219}$$

where k is the number of factors and N is the number of experiments in the design matrix.

The first property expressed by Eq. (II-217) is called the *property of orthogonality*, that is, the equality of the scalar products of all column vectors to zero. This property materially reduces the difficulties in the estimation of coefficients for the regression equation because the cofficient matrix (X^*X) of normal equations becomes diagonal, and its diagonal elements are equal to the number of experiments, N, in the design matrix. The diagonal elements of the inverse matrix $(X^*X)^{-1}$ are

$$C_{jj} = 1/N$$

Thus,

$$B = \begin{bmatrix} b_0 \\ b_1 \\ \cdot \\ \cdot \\ \cdot \\ b_k \end{bmatrix} = (X^*X)^{-1} X^*Y = \begin{bmatrix} 1/N & & & 0 \\ & 1/N & & \\ & & & \\ & & & \\ 0 & & & 1/N \end{bmatrix} \begin{bmatrix} \sum x_{0i} y_i \\ \sum x_{1i} y_i \\ \cdot \\ \cdot \\ \cdot \\ \sum x_{ki} y_i \end{bmatrix}$$

$$= \begin{bmatrix} \dfrac{\sum x_{0i} y_i}{N} \\ \dfrac{\sum x_{1i} y_i}{N} \\ \cdot \\ \cdot \\ \cdot \\ \dfrac{\sum x_{ki} y_i}{N} \end{bmatrix} \tag{II-220}$$

As a consequence, any coefficient b_j of the regression equation is defined by the scalar product of a y column by the respective x_j column divided into the number of experiments N in the design matrix:

$$b_j = \frac{1}{N} \sum_{i=1}^{N} x_{ji} y_i \tag{II-221}$$

Using the design presented in Table II-9, we first find the coefficients of the estimated linear regression equation

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 \qquad \text{(II-222)}$$

For example, b_1 can be determined by multiplying together the x_1 and y columns and adding together the products:

$$\begin{matrix} x_1 \\ \begin{bmatrix} -1 \\ +1 \\ -1 \\ +1 \\ -1 \\ +1 \\ -1 \\ +1 \end{bmatrix} \end{matrix} \times \begin{matrix} y \\ \begin{bmatrix} 2 \\ 6 \\ 4 \\ 8 \\ 10 \\ 18 \\ 8 \\ 12 \end{bmatrix} \end{matrix} = \begin{bmatrix} -2 \\ +6 \\ -4 \\ +8 \\ -10 \\ +18 \\ -8 \\ +12 \end{bmatrix}$$

$$\sum_{i=1}^{8} x_{1i} y_i = 20$$

$$b_1 = \frac{\sum_{i=1}^{8} x_{1i} y_i}{N} = \frac{20}{8} = +2.5$$

Similarly,

$$b_0 = 18.5 \quad b_2 = -0.5 \quad b_3 = +3.5$$

In the case of a fuller regression equation containing interaction coefficients

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 \qquad \text{(II-223)}$$

where one has to determine b_{12}, b_{13} and b_{23} (the second-order interaction terms) and b_{123} (the third-order interaction terms), the design matrix has to be extended as shown in Table II-10.

Table II-10

N	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	y
1	+1	−1	−1	−1	+1	+1	+1	−1	2
2	+1	+1	−1	−1	−1	−1	+1	+1	6
3	+1	−1	+1	−1	−1	+1	−1	+1	4
4	+1	+1	+1	−1	+1	−1	−1	−1	8
5	+1	−1	−1	+1	+1	−1	−1	+1	10
6	+1	+1	−1	+1	−1	+1	−1	−1	18
7	+1	−1	+1	+1	−1	−1	+1	−1	8
8	+1	+1	+1	+1	+1	+1	+1	+1	12

The interaction terms are determined in the same manner as the linear terms. To find b_{12}:

$$\begin{matrix} x_1x_2 \\ \begin{bmatrix} +1 \\ -1 \\ -1 \\ +1 \\ +1 \\ -1 \\ -1 \\ +1 \end{bmatrix} \end{matrix} \times \begin{matrix} y \\ \begin{bmatrix} 2 \\ 6 \\ 4 \\ 8 \\ 10 \\ 18 \\ 8 \\ 12 \end{bmatrix} \end{matrix} = \begin{bmatrix} +2 \\ -6 \\ -4 \\ +8 \\ +10 \\ -18 \\ -8 \\ +12 \end{bmatrix}$$

$$\sum_{i=1}^{8} (x_1x_2)_i y_i = -4$$

$$b_{12} = \frac{\sum_{i=1}^{N} (x_1x_2)_i y_i}{N} = -\frac{4}{8} = -0.5$$

The remaining coefficients are found in a similar manner

$$b_{13} = +0.5 \quad b_{23} = -1.5 \quad b_{123} = 0.25$$

By making replicate observations, it will be possible to determine s_e^2, to test the significance of the regression coefficients and, in the case of degrees of freedom, also the adequacy of the equation.

Since the correlation matrix $(X^*X)^{-1}$ for a designed experiment (Table II-6) is a diagonal matrix,

$$(X^*X)^{-1} = \begin{bmatrix} 1/N & & & 0 \\ & 1/N & & \\ & & \ddots & \\ 0 & & & 1/N \end{bmatrix}$$

the coefficients of the regression equation are uncorrelated. The significance of each coefficient can be tested on the basis of the Student t-test. Removal of an insignificant coefficient from the regression equation, Eq. (II-223), will have no effect on the remaining coefficients. Thus, the sample coefficients b_j prove to be *unconfounded estimates* for the respective general coefficients β_j

$$b_j \to \beta_j \tag{II-224}$$

that is, the coefficients of the regression equation describe the contribution of each factor to y.

The diagonal elements of a correlation matrix are equal to one another,

and so all coefficients in Eqs. (II-223) and (II-224) can be determined with the same accuracy:

$$s_{b_j} = s_e/\sqrt{N} \tag{II-225}$$

For example, three replicate observations have been made at the centre point to yield the following values: $y_1^0 = 8$, $y_2^0 = 9$, and $y_3^0 = 8.8$. Hence

$$\bar{y}^0 = \frac{\sum_{i=1}^{3} y_i^0}{3} = 8.6$$

$$s_e^2 = \frac{\sum_{i=1}^{3} (y_i^0 - \bar{y}^0)^2}{2} = 0.28$$

$$s_e = 0.55$$

$$s_{b_j} = \frac{0.55}{\sqrt{8}} = 0.2$$

The significance of the coefficients can be tested, using the Student t-test:

$$t_0 = \frac{|b_0|}{s_{b_0}} = \frac{8.5}{0.2} = 42.5 \qquad t_1 = \frac{|b_1|}{s_{b_1}} = \frac{2.5}{0.2} = 12.5$$

$$t_2 = \frac{|b_2|}{s_{b_2}} = 2.5 \qquad t_3 = \frac{|b_3|}{s_{b_3}} = 17.5$$

$$t_{12} = \frac{|b_{12}|}{s_{b_{12}}} = 2.5 \qquad t_{13} = \frac{|b_{13}|}{s_{b_{13}}} = 2.5$$

$$t_{23} = \frac{|b_{23}|}{s_{b_{23}}} = 7.5 \qquad t_{123} = \frac{|b_{123}|}{s_{b_{123}}} = 1.25$$

For a significance level of $p = 0.05$ and $f = 2$ degrees of freedom, the tabulated value of the Student t-distribution is $t_p(f) = 4.3$. Thus, the coefficients b_2, b_{12}, b_{13} and b_{123} are insignificant, and they must be removed from the equation. After removal of insignificant coefficients, the regression equation takes the form

$$\hat{y} = 8.5 + 2.5x_1 + 3.5x_3 - 1.5x_2x_3 \tag{II-226}$$

Now the estimated regression equation is tested to see how it fits the observations, using Fisher's test, that is, the variance ratio, $F = s_r^2/s_e^2$ where

$$s_r^2 = \frac{\sum_{i=1}^{8} (y_i - \hat{y}_i)^2}{N - l} = \frac{6}{4} = 1.5$$

$$s_e^2 = 0.28$$

where $l = 4$ is the number of significant coefficients in the regression equation. Then

$$F = 1.5 \div 0.28 = 5.3$$

The tabulated value of Fisher's F^{23} for $p = 0.05$, $f_1 = 4$ and $f_2 = 2$ is

$$F_p(f_1, f_2) = 19.3$$

Thus, $F < F_p(f_1, f_2)$, and Eq. (II-226) fits the experiment.

Fractional replicates. If, in developing a regression equation, one may limit oneself to a linear approximation, the amount of experimentation needed may be cut down by using a so-called *fractional factorial design*, or a *fractional replicate* of a full factorial design. If a fractional replicate is to be an orthogonal design in itself, the nearest full factorial design should be taken as a replicate. The number of observations should then be greater than that of unknown coefficients in the regression equation. Suppose we seek a linear approximation for a small area on the response surface with three independent factors

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3$$

Four observations may be sufficient to solve this problem, if the x_1x_2 column in the 2^2 factorial design (Table II-11) is used as a design for x_3 (Table II-12).

Table II-11

N	x_0	x_1	x_2	x_1x_2
1	+1	+1	+1	+1
2	+1	−1	−1	+1
3	+1	−1	+1	−1
4	+1	+1	−1	−1

Table II-12

N	x_0	x_1	x_2	x_3
1	+1	+1	+1	+1
2	+1	−1	−1	+1
3	+1	−1	+1	−1
4	+1	+1	−1	−1

This is known as the *half-replicate* of a full two-level factorial design for three variables, 2^3. This design is satisfactory for estimating the free term and the three coefficients of linear terms in the regression equation.

In practice, the equality of interaction terms to zero cannot be postulated *a priori*. However, there may be grounds for assuming that they are negli-

gible in comparison with the linear terms. If the regression coefficients of the paired products are non-zero, the estimated coefficients are *confounded estimates* of the general coefficients:

$$\left.\begin{aligned} b_1 &\rightarrow \beta_1+\beta_{23} \\ b_2 &\rightarrow \beta_2+\beta_{13} \\ b_3 &\rightarrow \beta_3+\beta_{12} \end{aligned}\right\} \qquad \text{(II-227)}$$

where the β's are the expected values of the respective coefficients.

These general coefficients cannot be estimated separately on the basis of a design envisaging as few as four observations (Table II-12), because there is no way to distinguish between the columns for linear terms and paired products. If, for example, in addition to the columns in Table II-12, we evaluate one more column for the product x_1x_3, we shall see that the elements of this column are identically equal to the elements of the x_2-column. Thus, a cut-down in the amount of experimentation results in the appearance of confounded estimates of the coefficients. In order to determine which general coefficients are confounded, it is convenient to substitute x_3 for x_1x_2 (see Table II-11) to obtain

$$x_3 = x_1x_2 \qquad \text{(II-228)}$$

known as the *generating relation*. Multiplying both sides of the generating relation by x_3 gives

$$x_3^2 = x_1x_2x_3$$

What we have got on the right-hand side is a unit column

$$1 = x_1x_2x_3 \qquad \text{(II-229)}$$

The product, Eq. (II-229), is called the *defining contrast*. It readily identifies the columns containing like elements.

Multiplying the defining contrast in turn by x_1, x_2 and x_3, we get

$$\begin{aligned} x_1 &= x_1^2x_2x_3 = x_2x_3 \\ x_2 &= x_1x_3 \\ x_3 &= x_1x_2 \end{aligned} \qquad \text{(II-229}a\text{)}$$

The above relations (II-229*a*) correspond to a system of confounded estimates (II-227).

When use is made of a fractional factorial design, we must have a clear idea about the so-called *resolving power* of the fractional replicate, that is, know in advance which coefficients are unconfounded estimates of the respective general coefficients. Then, according to the objective sought, we can select a fractional replicate which will yield a maximum amount of information from the experiment.

For example, in the case of a fractional design for four factors $k = 4$, the generating relation may be one of the form

$$x_4 = x_1x_2x_3 \qquad \text{(II-230)}$$

and any of the second-order interaction terms, say,

$$x_4 = x_1x_2 \qquad \text{(II-231)}$$

The design matrix for the generating relation, Eq. (II-230), is given in Table II-13.

Table II-13

N	x_0	x_1	x_2	x_3	x_4
1	+1	+1	+1	+1	+1
2	+1	−1	−1	+1	+1
3	+1	−1	+1	+1	−1
4	+1	+1	−1	+1	−1
5	+1	+1	+1	−1	−1
6	+1	−1	−1	−1	−1
7	+1	−1	+1	−1	+1
8	+1	+1	−1	−1	+1

Using the defining contrast $1 = x_1x_2x_3x_4$, we get the following system of joint estimates:

$$\begin{aligned}
x_1 &= x_2x_3x_4 & b_1 &\rightarrow \beta_1+\beta_{234}\\
x_2 &= x_1x_3x_4 & b_2 &\rightarrow \beta_2+\beta_{134}\\
x_3 &= x_1x_2x_4 & b_3 &\rightarrow \beta_3+\beta_{124}\\
x_4 &= x_1x_2x_3 & b_4 &\rightarrow \beta_4+\beta_{123}\\
x_1x_2 &= x_3x_4 & b_{12} &\rightarrow \beta_{12}+\beta_{34}\\
x_1x_3 &= x_2x_4 & b_{13} &\rightarrow \beta_{13}+\beta_{24}\\
x_1x_4 &= x_2x_3 & b_{14} &\rightarrow \beta_{14}+\beta_{13}
\end{aligned} \qquad \text{(II-232)}$$

In practice, third-order interactions are equal to zero more often than second-order interactions. In other words, if we are interested more in the estimates of the linear terms, we should preferably use the generating relation

$$x_4 = x_1x_2x_3$$

With a generating relation of the form given by Eq. (II-231), the design matrix will be as shown in Table II-14.

The defining contrast is defined by

$$1 = x_1x_2x_4$$

Table II-14

N	x_0	x_1	x_2	x_3	x_4
1	+1	+1	+1	+1	+1
2	+1	−1	−1	+1	+1
3	+1	−1	+1	+1	−1
4	+1	+1	−1	+1	−1
5	+1	+1	+1	−1	+1
6	+1	−1	−1	−1	+1
7	+1	−1	+1	−1	−1
8	+1	+1	−1	−1	−1

Thus, we get the following system of estimates:

$$\begin{aligned}
x_1 &= x_2x_4 & b_1 &\to \beta_1+\beta_{24}\\
x_2 &= x_1x_4 & b_2 &\to \beta_2+\beta_{14}\\
x_3 &= x_1x_2x_3x_4 & b_3 &\to \beta_3+\beta_{1234}\\
x_4 &= x_1x_2 & b_4 &\to \beta_4+\beta_{12}\\
x_1x_3 &= x_2x_3x_4 & b_{13} &\to \beta_{13}+\beta_{234}\\
x_2x_3 &= x_1x_3x_4 & b_{23} &\to \beta_{23}+\beta_{134}\\
x_3x_4 &= x_1x_2x_4 & b_{34} &\to \beta_{34}+\beta_{124}
\end{aligned} \qquad \text{(II-233)}$$

Thus, it will be advantageous to use a fractional replicate with the generating relation $x_4 = x_1x_2$ (II-231), if our interest is mainly in the coefficients β_{13}, β_{23} and β_{34}.

Use is also made of replicates of higher fractional orders (one-fourth replicates, one-eighth replicates, etc.). Generally, a fractional replicate in which p linear terms are equated to interaction terms is designated 2^{k-p}.

Optimal two-level factorial designs for k and $(k-p)$ factors, 2^k and 2^{k-p}, designs offer the following advantages: the designs are orthogonal, and this makes all computations very simple; all coefficients are estimated independently of one another; each coefficient is estimated on the basis of all N observations; all regression coefficients are estimated to the same variance which is minimal. It should also be stressed that the linear 2^k and $2^{k-p}_{\hat{y}}$ designs have the property of *rotatability*. Since there is no correlation between the coefficients, then according to the rule of addition of variances in the case of a linear equation in k factors, we have:[23]

$$s^2_{\hat{y}} = s^2_{b_0}+x_1^2s^2_{b_1}+ \ldots +x_k^2s^2_{b_k} \qquad \text{(II-234)}$$

Since $s_{b_j}^2 = s_e^2/N$, then

$$s_{\hat{y}}^2 = (s_e^2/N)(1+x_1^2+ \ldots +x_k^2) = (s_e^2/N)(1+\rho^2) \qquad \text{(II-235)}$$

$$\rho^2 = \sum_{j=1}^{k} x_j^2$$

where ρ^2 is the square of the radius of the sphere in a k-dimensional space.

The reciprocal of $s_{\hat{y}}^2$ may be taken as a measure of the information contained in the regression equation.

According to (II-235), the amount of information decreases in proportion to the square of the radius of the sphere, ρ^2, and is the same for all equidistant points. Designs having this property are called *rotatable designs.*

Optimization by steepest ascent on a response surface. The objective of optimization may be stated as follows: we seek to determine the coordinates of an external point, $x_1^{opt}, x_2^{opt}, \ldots, x_k^{opt}$, on the response surface, $y = f(x_1, x_2, \ldots, x_k)$ (Fig. II-36). We construct contours of constant value of y, $y = \text{const}$, for $k = 2$ (Fig. II-37). In conventional experiments, it is customary to hold one of the factors, say x_1, constant and to move in the direction of the other factor, x_2, from point L. It is assumed that the coordinates of point L are known from previous observations. The motion in the x_2 direction continues until y increases no longer (Fig. II-37). At the point of the best

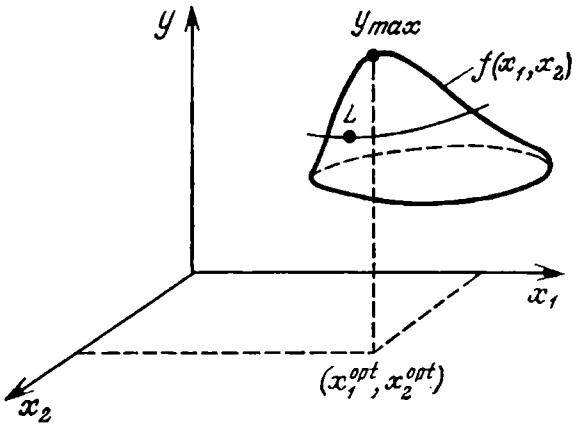


Fig. II-36. Response surface for $k = 2$

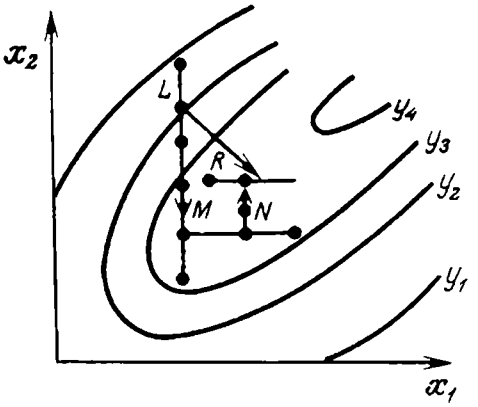


Fig. II-37. Contours on the response surface for $k = 2$

yield (M), x_2 is held constant, and the experimenter moves in the x_1 direction. At point N, x_1 is again held constant, and the motion is resumed in the x_2 direction, etc. It is obvious that the broken line $LMNR \ldots$ is not the shortest path to the optimum. As will be recalled, the shortest path to the optimum is that of steepest ascent, that is in the direction of the gradient, at right angles to the contours of constant values of y (shown by the dots in Fig. II-37). If, in the general case, the response surface is described by an equa-

tion of the form

$$y = f(x_1, x_2, \ldots, x_k)$$

then the gradient of the function will be defined by

$$\text{grad } f = \frac{\partial f}{\partial x_1}\vec{i} + \frac{\partial f}{\partial x_2}\vec{j} + \ldots + \frac{\partial f}{\partial x_k}\vec{k} \qquad \text{(II-236)}$$

where $i, j, \ldots, k$ are the unit vectors in the direction of the coordinate axes.

It is assumed that the function f is continuous, univalued and has no non-singular points.

Box and Wilson[29] have proposed a "step-by-step" procedure for advance on the response surface. The experimenter starts working by selecting a local region for experimentation in the vicinity of point L and describes the response surface by an estimated linear regression equation of the form

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2$$

Then he calculates the components of the gradient of y

$$\partial\hat{y}/\partial x_1 = b_1 \quad \partial\hat{y}/\partial x_2 = b_2$$

and moves on the response surface in the direction of the linear approximation gradient.

The relative step size should be proportional to the product of the coefficient b_j by the increment size, Δz_j, or $b_j \Delta z_j$. If one linear approximation proves insufficient, the experimenter selects a new local region for experimentation centered around a point where y is a maximum, and ascertains the direction of steepest ascent again. This "step-by-step" procedure is carried on until the experimenter finds himself in the vicinity of the extremum, or in the "nearly stationary" region.

Description of a "nearly stationary" region. In this region, the interaction and quadratic terms gain in significance. The closeness of the "nearly stationary" region can be ascertained by replicating the centre point of the design ($x_1 = 0, x_2 = 0, \ldots, x_k = 0$) and computing the mean, $\bar{y}^0$. The quantity $\bar{y}^0$ is an estimate of the free term of the theoretical regression equation, $\bar{y}^0 \to \beta_0$, while b_0 calculated in the fractional experiment by the equation

$$b_0 = \frac{\sum_{i=1}^{N} x_{0i} y_i}{N}$$

is a joint estimate of the free term and the sum of the quadratic terms

$$b_0 \to \beta_0 + \sum_{j=1}^{k} \beta_{jj}$$

if the theoretical regression equation is a second-order polynomial. There-

fore, the difference

$$b_0 - \bar{y}^0 \to \sum_{j=1}^{k} \beta_{jj} \qquad \text{(II-237)}$$

may to a certain extent serve as a measure of the curvature of the surface.

The "nearly stationary" region is described by nonlinear equations.

So far reliable designs have only been developed for second-order polynomials. Besides, second-order surfaces lend themselves to systematization. In order to describe the response surface by second-order polynomials, the factors in experimental designs should take at least three different values.

A full 3^k factorial design involves a very great number of observations

k	3	4	5
3^k	27	81	243

The number of observations can be reduced through the use of *composite* or *sequential designs* proposed by Box and Wilson.[29] The "kernel" of such a design is a full 2^k factorial design for $k < 5$ or its fractional replicate at $k \geqslant 5$. If the estimated linear regression equation fails the test for the adequacy of fit, it is necessary:

(1) to add $2k$ "star" points on the coordinate axes of factorial space $(\pm\alpha, 0, \ldots, 0)$, $(0, \pm\alpha, 0, \ldots, 0)$, $\ldots$, $(0, 0, \ldots, 0, \pm\alpha)$, where α is the distance from the centre point to a "star" point, or a "star" arm;

(2) to increase the number of observations, n_0, at the centre point of the design.

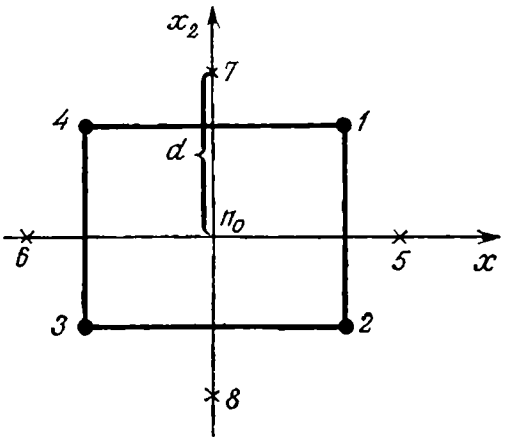


Fig. II-38. A composite design at $k = 2$

The total number of observations in the matrix of a composite design for k factors is given by

$$N = 2^k + 2k + n_0 \qquad k < 5$$
$$N = 2^{k-1} + 2k + n_0 \qquad k \geqslant 5 \qquad \text{(II-238)}$$

Consider a composite design, using an example, for $k = 2$ (Fig. II-38). Points *1*, *2*, *3*, and *4* form a full two-level factorial design for two factors, while points *5*, *6*, *7* and *8* are "star" points with coordinates $(\pm\alpha, 0)$ and $(0, \pm\alpha)$, the observations at the centre point, n_0, have zero coordinates, $(0, 0)$.

The magnitude of the star arm, α, and the number of observations at the centre point, n_0, depend on the design selected.

Orthogonal second-order designs. Composite designs can readily be reduced to the orthogonal form by an appropriate selection of the star arm,

α. At the same time, no constraints are imposed on the number n_0 of observations at the centre point, and n_0 is usually equated to unity.

Putting $n_0 = 1$, the matrix of a composite design for $k = 2$ (Fig. II-38) will be as shown in Table II-15.

Table II-15

N	x_0	x_1	x_2	x_1x_2	x_1^2	x_2^2
1	+1	+1	+1	+1	+1	+1
2	+1	+1	−1	−1	+1	+1
3	+1	−1	−1	+1	+1	+1
4	+1	−1	+1	−1	+1	+1
5	+1	+α	0	0	α^2	0
6	+1	−α	0	0	α^2	0
7	+1	0	+α	0	0	α^2
8	+1	0	−α	0	0	α^2
9	+1	0	0	0	0	0

Generally, the above matrix is non-orthogonal because

$$\sum_{i=1}^{N} x_{0i}x_{ji}^2 \neq 0$$
$$\sum_{i=1}^{N} x_{ji}^2 x_{ui}^2 \neq 0 \qquad \text{(II-239)}$$

The matrix of Table II-15 can be transformed to the orthogonal form as follows. To begin with, we transform the quadratic variables

$$x_j' = x_j^2 - \frac{\sum_{i=1}^{N} x_{ji}^2}{N} = x_j^2 - \bar{x}_j^2 \qquad \text{(II-240)}$$

Also,

$$\sum_{j=1}^{N} x_{0i}x_{ji}' = \sum_{i=1}^{N} x_{ij}^2 - N\bar{x}_j^2 = 0 \qquad \text{(II-241)}$$

$$\sum_{i=1}^{N} x_{ji}'x_{ui}' \neq 0 \qquad \text{(II-242)}$$

To make the design matrix fully orthogonal, the star arm, α, is selected so as to reduce to zero the non-diagonal term of the correlation matrix $(X^*X)^{-1}$. The values of α for different numbers of factors are listed in Table II-16.[26]

Table II-16

	Number of factors, k			
	2	3	4	5
Design "kernel"	2^2	2^3	2^4	2^{5-1} $x_5 = x_1x_2x_3x_4$
α	1.00	1.215	1.414	1.547

The orthogonal second-order matrix for $k = 2$ has the form (Table II-17):

Table II-17

N	x_0	x_1	x_2	x_1x_2	x_1^1	x_2^1
1	+1	+1	+1	+1	+1/3	+1/3
2	+1	+1	−1	−1	+1/3	+1/3
3	+1	−1	−1	+1	+1/3	+1/3
4	+1	−1	+1	−1	+1/3	+1/3
5	+1	+1	0	0	+1/3	−2/3
6	+1	−1	0	0	+1/3	−2/3
7	+1	0	+1	0	−2/3	+1/3
8	+1	0	−1	0	−2/3	+1/3
9	+1	0	0	0	−2/3	−2/3

Since the design matrix is orthogonal, all regression coefficients can be estimated independently of one another by the equation

$$b_j = \frac{\sum_{i=1}^{N} x_{ji} y_i}{\sum_{i=1}^{N} x_{ji}^2} \qquad \text{(II-243)}$$

and the estimates of the coefficient variance are the same:

$$s_{b_j}^2 = \frac{s_e^2}{\sum_{i=1}^{N} x_{ij}^2} \qquad \text{(II-244)}$$

As a result, the following estimated regression equation is derived from the matrix with transformed columns for the quadratic terms:

$$\hat{y} = b_0' + b_1x_1 + b_2x_2 + \ldots + b_kx_k + b_{12}x_1x_2 + \ldots + b_{(k-1)k}x_{k-1}x_k + b_{11}(x_1^2 - \bar{x}_1^2) + \ldots + b_{kk}(x_k^2 - \bar{x}_k^2) \qquad \text{(II-245)}$$

To change back to normal notation, b_0 is found from

$$b_0 = b_0' - b_{11}\bar{x}_1^2 - \ldots - b_{kk}\bar{x} \qquad \text{(II-246)}$$

and estimated with a variance equal to

$$s_{b_0}^2 = s_{b_0'}^2 + (\bar{x}_1^2)^2 s_{b_{11}}^2 + \ldots + (\bar{x}_k)^2 s_{b_{kk}}^2 \qquad \text{(II-247)}$$

Knowing the error mean square, one can test the equation

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + \ldots + b_kx_k + b_{12}x_1x_2 + \ldots$$
$$+ b_{(k-1)k}x_{(k-1)}x_k + b_{11}x_1^2 + \ldots + b_kx_k^2$$

for the significance of its coefficients and for the adequacy of fit.

The estimated regression equation is tested for the adequacy of fit, using the Fisher F-test, that is, $F = s_r^2/s_e^2$. The equation fits the experimental data, if the variance ratio thus formed is smaller than the tabulated value of F for the significance level p (usually, 0.05) and the numbers of degrees of freedom for the residual and error variances:

$$F < F_p(f_1, f_2)$$

where $f_1 = N - l$ is the number of degrees of freedom for the residual variance, f_2 is the number of degrees of freedom for the error variance, N is the number of observations in the design matrix, and l is the number of coefficients in the estimated second-order regression equation.

For k factors

$$l = (k+1) + k + C_k^2 = (k+1) + k + \frac{k!}{2!\,(k-2)!} \qquad \text{(II-248)}$$

where C_k^2 is the number of combinations of k factors taken two at a time and equal to the number of second-order interaction terms in Eq. (II-245).

The coefficients are tested for significance, using the Student t-test, $t_j = b_j/s_{b_j}$. A coefficient is significant, if $t_j > t_{p=0.05}(f_2)$, where f_2 is the number of degrees of freedom for the estimate of the error variance.

The coefficients of estimated regression equations derived by means of orthogonal second-order designs are estimated to a varying degree of accuracy, see Eq. (II-244). In contrast, first-order orthogonal designs ensure an equal accuracy of estimation for all coefficients.

Second-order rotatable designs. A second-order orthogonal design is not rotatable, and, as a consequence, the errors in y at experimental points on the response surface may be smaller than they are in the case of determinations from a regression equation.

Box and Hunter[30] have proposed a rotatable second-order design. For a central composite design to be rotatable, the star arm α is chosen from the condition such that

$$\alpha = 2^{k/4} \quad \alpha = 2^{(k-1)/4}$$

The number n_0 of observations at the centre point is increased (the centre point is said to be replicated) so as to make the matrix X^*X non-degenerate.

The values of α and n_0 for different numbers of factors k, are given in Table II-18.

Table II-18

	Number of factors, k								
	2	3	4	5	6	6	6	7	7
Design "kernel"	2^2	2^3	2^4	2^5	2^{5-1}	2^6	2^{6-1}	2^7	2^{7-1}
α	1.414	1.682	2.00	2.378	2.00	2.828	2.378	3.333	2.828
n_0	5	6	7	10	6	15	9	21	14

The matrix of a second-order rotatable design for $k = 2$ is given below (Table II-19).

Table II-19

N	x_0	x_1	x_2	x_1x_2	x_1^2	x_2^2
1	+1	+1	+1	+1	+1	+1
2	+1	+1	−1	−1	+1	+1
3	+1	−1	−1	+1	+1	+1
4	+1	−1	+1	−1	+1	+1
5	+1	+1.414	0	0	2	0
6	+1	−1.414	0	0	2	0
7	+1	0	+1.414	0	0	2
8	+1	0	−1.414	0	0	2
9	+1	0	0	0	0	0
10	+1	0	0	0	0	0
11	+1	0	0	0	0	0
12	+1	0	0	0	0	0

The matrix of a second-order rotatable design is non-orthogonal because

$$\sum_{i=1}^{N} x_{0i}x_{ji}^2 \neq 0$$

$$\sum_{i=1}^{N} x_{ji}^2 x_{ui}^2 \neq 0$$

The b_{jj} coefficients are cross-correlated and correlated with the free term, b_0. Therefore, in order to estimate the coefficients of the regression equation, one needs to solve a system of simultaneous normal equations by inversion

of matrix X^*X:

$$B = (X^*X)^{-1}XY$$

$$s_{b_j}^2 = c_{jj}s_e^2 \tag{II-249}$$

where c_{jj} is the respective diagonal element of the correlation matrix, $(X^*X)^{-1}$.

In view of the specific feature of matrix X^*X it is possible in rotatable designs to solve the matrix equation, Eq. (II-249), generally and to derive equations for the estimation of regression coefficients and of their variances:

$$b_0 = \frac{A}{N}\left[2\lambda_4^2(k+2)(0y) - 2\lambda_4 C\sum_{j=1}^{k}(jjy)\right] \tag{II-250}$$

$$b_j = \frac{C}{N}(jy) \tag{II-251}$$

$$b_{jj} = \frac{A}{N}\left[C^2[(k+2)\lambda_4 - k](jjy) + C^2(1-\lambda_4)\sum_{j=1}^{k}(jjy) - 2\lambda_4 C(0y)\right] \tag{II-252}$$

$$b_{uj} = \frac{C^2}{N\lambda_4}(ujy) \tag{II-253}$$

$$s_{b_0}^2 = \frac{2A\lambda_4^2(k+2)}{N}s_e^2 \tag{II-254}$$

$$s_{b_j}^2 = \frac{C}{N}s_e^2 \tag{II-255}$$

$$s_{b_{jj}}^2 = \frac{A[(k+1)\lambda_4 - (k-1)]C^2}{N}s_e^2 \tag{II-256}$$

$$s_{b_{uj}}^2 = \frac{C^2}{\lambda_4 N}s_e^2 \tag{II-257}$$

where

$$(0y) = \sum_{i=1}^{N} x_{0i}y_i \qquad (juy) = \sum_{i=1}^{N} x_{ji}x_{ui}y_i$$

$$(jy) = \sum_{i=1}^{N} x_{ji}y_i \qquad (jjy) = \sum_{i=1}^{N} x_{ji}^2 y_i$$

$$C = \frac{N}{\sum_{i=1}^{N} x_{ji}^2} \qquad A = \frac{1}{2\lambda_4[(k+2)\lambda_4 - k]}$$

$$\lambda_4 = \frac{Nk\sum_{i=1}^{s} n_i\rho_i^4}{(k+2)\left(\sum_{i=1}^{s} n_i\rho_i^2\right)^2} \tag{II-258}$$

In the last equations, s is the number of spheres described around the centre point of the design, ρ is the radius of the sphere, n is the number of

points lying on the sphere of radius ρ, and N is the total number of points in a rotatable design defined by

$$\sum_{i=1}^{s} n_i = N$$

With second-order rotatable designs, no replication is needed in order to find the error mean square. Instead, this can be done by replicating the centre point. Accordingly, the estimated regression equation derived from a second-order rotatable design is tested for the adequacy of fit as follows.

To begin with, one finds the residual sum of squares

$$S_1 = \sum_{i=1}^{N} (y_i - \hat{y}_i)^2$$

for which the number of degrees of freedom is

$$f_1 = N - l = N - \frac{(k+2)(k+1)}{2}$$

From repeated observations at the centre point, one then finds the error sum of squares

$$S_2 = \sum_{i=1}^{n_0} (y_{0i} - \bar{y}_0)^2$$

for which the number of degrees of freedom is

$$f_2 = n_0 - 1$$

The next step is to find the inadequacy of fit sum of squares

$$S_3 = S_1 - S_2$$

for which the number of degrees of freedom is given by

$$f_3 = f_1 - f_2 = N - \frac{(k+2)(k+1)}{2} - (n_0 - 1)$$

Then an F-test is applied to test the adequacy of fit:

$$F = \frac{S_3/f_3}{S_2/f_2}$$

The estimated regression equation fits the data adequately if

$$F < F_{p=0.05(f_3, f_2)}$$

The significance of the estimated coefficients is tested, using the Student t-test. If one of the quadratic terms turns out to be insignificant, it should be removed, and the coefficients of the regression equation must be estimated anew.

Canonical analysis of the response surface. An estimated second-order regression equation which adequately fits the "nearly stationary" region is then analysed to determine the coordinates of the optimum. The usual

procedure in this case is to transform the second-order polynomial derived from the experimental data into a standard, canonical equation.[26]

Consider an estimated regression equation in two factors:

$$\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 + b_{11} x_1^2 + b_{22} x_2^2 \qquad \text{(II-259)}$$

Its canonical form is

$$\hat{y} - \hat{y}_S = B_{11} X_1^2 + B_{22} X_2^2 \qquad \text{(II-260)}$$

where $\hat{y}_S$ is the value of the predicted response at the centre of the response surface, S.

Equation (II-259) is transformed to its canonical form, Eq. (II-260), in two steps. Firstly, the origin of coordinates is translated to the extremum of the response surface, point S, so as to get rid of the linear, or first-order, terms. Secondly, the coordinate axes are rotated through an angle to get rid of the interaction, or cross-product, terms.

On the basis of canonical equations, one can evaluate the nature of response surfaces as follows:

(1) If B_{11} and B_{22} have the same sign, and are unequal, the response surface is an elliptical paraboloid. On passing planes of constant value, $\hat{y} = \text{const}$, through the response surface, we obtain ellipses (Fig. II-39*a*). The centre of the figure, S, is a maximum if B_{11} and B_{22} are negative, and a minimum if they are positive.

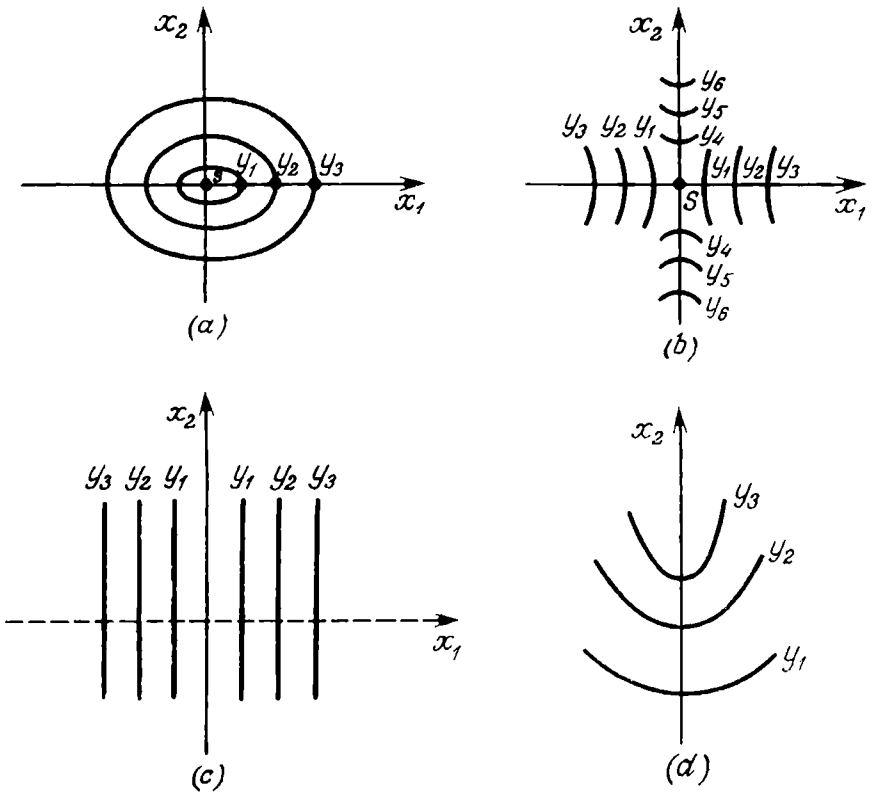


Fig. II-39. Response surface for canonic equations

(2) If B_{11} and B_{22} have unlike signs, the response surface is a hyperbolic paraboloid (a saddle). Planes passing through the response surface produce hyperbolas (Fig. II-39*b*). At S is a minimax point.

(3) If one of the coefficients is equal to zero, $B_{22} = 0$, and the other is negative, the response surface is a stationary ridge (Fig. II-39*c*), and the surface has no centre.

(4) If one of the coefficients, B_{22}, is equal to zero and the centre is at infinity, translation of the origin of coordinates to an applicable point near the centre of the design produces the equation of a parabola (Fig. II-39*d*):

$$\hat{y} - \hat{y}_S = B_{11}X_1^2 + B_2X_2$$

and the response surface is a rising ridge.

In the case of a minimax (saddle point) the extremum can be found by methods of nonlinear programming.

Regular simplex designs. Quite recently, a number of studies[31-33] have appeared, proposing the use of regular simplex designs in the ascent phase.

A *regular simplex* is defined as a set of $k+1$ equidistant points in k-dimensional space. In one-dimensional space, that is for one factor, a regular simplex is a straight-line segment (two points), for two factors a regular simplex is an equilateral triangle (three points), for three factors the design is a regular tetrahedron (four points), etc.

In the search for an optimum, trial values of the experimental factors can be selected at points in multidimensional factor space located at the vertices of the regular simplex. After the first cycle of observations, the vertex associated with the conditions yielding the poorest response is identified. This point is now deleted, and a new point which is a mirror reflection from the opposite face of the simplex is added (a *face* is a set of k points of a k-dimensional simplex). This new point and the remain-

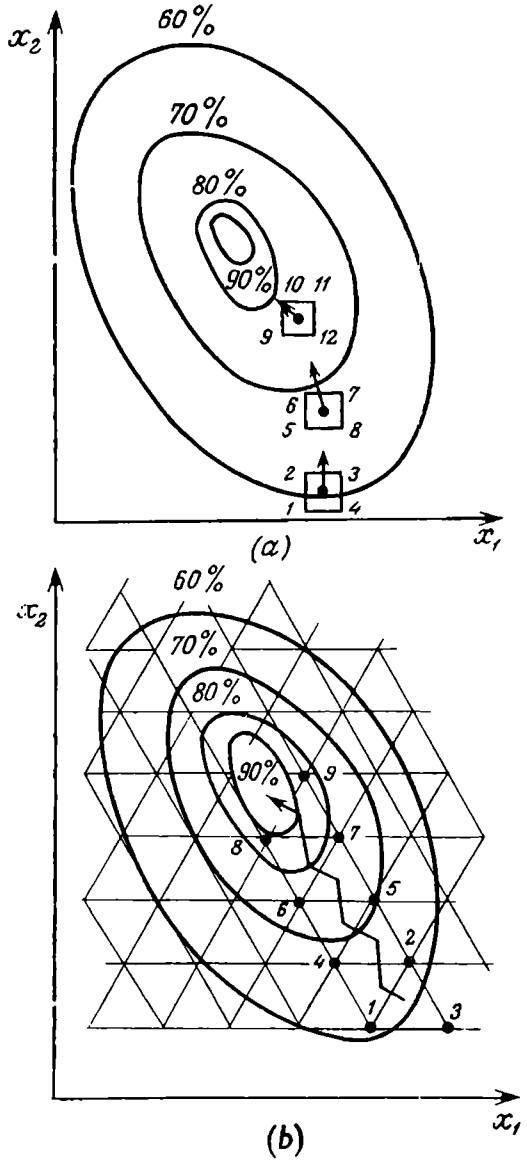


Fig. II-40. Patterns of advance to the optimum area
(*a*) steepest ascent; (*b*) regular simplex method

ing old points form a new regular simplex, termed a reflection, in which the centroid is displaced in the direction from the poorest-response point towards the centroid of the remaining points. In the general case, this direction is not the path of steepest ascent; yet, it points towards a better performance of the process.

Continuation of this procedure, always deleting the point that yields the poorest response and replacing it with a mirror image, leads to a nearly stationary region.

In Fig. II-40 the reader can see geometric interpretations for (a) the conventional method of steepest ascent and (b) the regular simplex method in which the trajectory is a broken line oscillating about the path of steepest ascent. Although the path is broken, the number of moves needed to reach the optimum region may be small. This is because $k+1$ observations have to be made only at the beginning; after that, every move involves one additional observation under conditions selected from an analysis of the previous observations.

It can be shown that with the dimensionless variables arranged in matrix X

$$X = \begin{bmatrix} x_1 & x_2 & \dots & x_j & \dots & x_{k-1} & x_k \\ -x_1 & x_2 & & x_j & & x_{k-1} & x_k \\ 0 & -2x_2 & & x_j & & x_{k-1} & x_k \\ & & & \cdot & & \cdot & \cdot \\ \cdot & \cdot & & \cdot & & \cdot & \cdot \\ 0 & 0 & & -jx_j & & x_{k-1} & x_k \\ & & & \cdot & & \cdot & \cdot \\ & & & \cdot & & & \cdot \\ 0 & 0 & & 0 & & -(k-1)x_{k-1} & x_k \\ 0 & 0 & & 0 & & 0 & -kx_k \end{bmatrix} \tag{II-261}$$

where

$$x_j = \sqrt{\frac{1}{2j(j-1)}} \tag{II-262}$$

the points of the matrix will form a regular k-dimensional simplex with the centre at the origin of coordinates and with an edge of unity. The height of this simplex (that is, the distance from a vertex to the opposite face) is

$$h_j = \frac{j+1}{\sqrt{2j(j+1)}} \tag{II-263}$$

The number of observations in a simplex matrix for k factors is $N = k+1$, which is equal to the number of coefficients in the regression equation. This is why simplex designs are called saturated.

The matrix satisfies the condition

$$\sum_{i=1}^{N} x_{ji}x_{li} = 0 \quad j \neq l; \quad j, l = 1, 2, \ldots, k$$

$$\sum_{i=1}^{N} x_{ji} = 0$$

but fails to satisfy the condition

$$\sum_{i=1}^{N} x_{ji}^2 = N$$

For any jth column

$$\sum_{i=1}^{N} x_{ij}^2 = j\,\frac{1}{2j(j+1)} + j^2\,\frac{1}{2j(j+1)} = 0.5 \qquad \text{(II-264)}$$

Therefore, for a simplex design the correlation matrix $(X^*X)^{-1}$ has the form

$$(X^*X)^{-1} = \begin{bmatrix} 1/N & & & & \\ & 2 & & & \\ & & 2 & & 0 \\ & & & \ddots & \\ & & & & \ddots \\ 0 & & & & 2 \end{bmatrix} \qquad \text{(II-265)}$$

and the regression coefficients are estimated by the equations

$$b_0 = \frac{\sum_{i=1}^{N} y_i}{N} \qquad b_j = 2\sum_{i=1}^{N} x_{ji}y_i \quad j = 1, 2, \ldots, k$$

Simplex designs are rotatable designs. A major drawback of simplex designs is the lack of *d-optimality*, a property possessed by designs with a minimum value for the determinant of the correlation matrix, $[(X^*X)^{-1}]$, for a given number N of observations.

With orthogonal designs, the estimated variance of coefficients is given by

$$s_{b_j}^2 = \frac{s_e^2}{\sum_{i=1}^{N} x_{ji}^2}$$

With simplex designs,

$$s_{b_j}^2 = \frac{s_e^2}{0.5} = 2s_e^2 \qquad \text{(II-266)}$$

For an optimum two-level design,

$$s_{b_j}^2 = \frac{s_e^2}{N}$$

Thus, the estimated variance of coefficients for ± 1 designs is less than it is for simplex designs.

Saturated designs of the ± 1 type can be constructed only for cases where the number of factors is $4l-1$, where l is a positive integer. For example, for $k = 3, 7, 15$, and 31, these will be fractional replicates of a full factorial design.

To facilitate the practical use of the simplex matrix, the numerical values have been calculated for its elements in advance:

$$X = \begin{bmatrix} 0.5 & 0.289 & 0.204 & 0.158 & 0.129 & 0.109 \\ -0.5 & 0.289 & 0.204 & 0.158 & 0.129 & 0.109 \\ 0 & -0.578 & 0.304 & 0.158 & 0.129 & 0.109 \\ 0 & 0 & -0.612 & 0.158 & 0.129 & 0.109 \\ 0 & 0 & 0 & -0.632 & 0.129 & 0.109 \\ 0 & 0 & 0 & 0 & -0.645 & 0.109 \\ 0 & 0 & 0 & 0 & 0 & -0.655 \end{bmatrix} \quad \text{(II-267)}$$

In dimensionless form, an experimental design for k factors consists of k columns and $k+1$ rows in matrix X. As already explained, experimental optimization proceeds by constructing a new simplex on the face of the old one, opposite the worst point. The new point added to the simplex is the location of the new experiment: hence, the design incorporates the old experiments and a new one on each move. To find the coordinates of the added vertex, take twice the average of all the coordinates of the common points (those retained in the simplex) and subtract the coordinates of the deleted vertex. In mathematical form:

$$x_j^{(k+2)} = 2x_j^{(c)} - x_j^{(l)} \quad j = 1, 2, \ldots, k \qquad \text{(II-268)}$$

where $x_j^{(l)}$ is the jth coordinate of the deleted vertex, $x_j^{(k+2)}$ is the jth coordinate of the added vertex, and $x_j^{(c)}$ is the jth coordinate of the centre on the opposite face, defined as

$$x_j^{(c)} = \frac{\sum_{i=1}^{k+1} x_j^{(i)}}{k} \quad i \neq l \qquad \text{(II-269)}$$

The original k-dimensional simplex may be completed to a $(k+1)$-dimensional simplex by adding one more vertex. The need for this arises when a process was examined as one dependent on k factors, while actually it depends on $(k+1)$ factors. For some reason, the value of the $(k+1)$st factor was not varied in the experiment. Thus, all vertices of the k-dimensional simplex are in effect the vertices of a $(k+1)$-dimensional simplex, located in a hyperplane $x_{k+1} = d$, where d is a fixed value of the $(k+1)$st factor in dimensionless form. From geometric considerations it follows that in order to construct a $(k+1)$-dimensional simplex from a k-dimensional one, it is necessary to locate the centroid of the k-dimensional simplex in $(k+1)$-dimensional space and to erect through this point a perpendicular to the

hyperplane in which the vertices of the k-dimensional simplex are located. Laying off a segment h_{k+1} long (which is the height of the $(k+1)$-dimensional simplex) will locate a point on the perpendicular: this point together with the old vertices will form a $(k+1)$-dimensional simplex. The coordinates of the new vertex are: $x_1^{(0)}, x_2^{(0)}, \ldots, x_j^{(0)}, \ldots, x_k^{(0)}, d+h_{k+1}$, where $x_j^{(0)}$ is the jth coordinate of the centre in the old simplex. With conventional factorial designs, adding one more factor doubles the number of observations required.

Another advantage of the regular simplex method is that the constraints on the approximation of the response surface with a hyperplane are not so stringent as they are with the Box-Wilson (gradient) method. Also, the observations may be less accurate, because an error in ranking the results will only make the path of ascent longer. Besides, several optimizing factors may be considered in regular simplex designs simultaneously.

Evolutionary operation (EVOP). Evolutionary planning proposed by Box[34] makes use of small changes in operating conditions, whose effect on the output of the process is likewise small but which are repeated many times until the general effect of the many small changes becomes noticeable. This technique is especially applicable to experimentation under conditions of a large factory, department or installations where large perturbations might yield uneconomic or dangerous operating conditions. The term "evolutionary" has been adopted because of the resemblance of the technique with biological evolution where natural selection proceeds by small mutations.

Cybernetically, an evolutionary operation is an example of feedback process control.

With the EVOP technique, the process under study is broken down into a series of phases each consisting of a repeated cycle. Each cycle is repeated again and again under the same set of operating conditions or the levels of independent variables (Fig. II-41). Each cycle may comprise a full or a fractional factorial design. At the end of each phase, the observations are analysed and a decision taken on a new set of operating conditions. The number n of cycles, or replication, is chosen so as to facilitate the detection of small differences between the normal process and the perturbed process, because the result of each small change wallows in a sea of noise. In this, use is made of the conventional error accumulation method according to which the error in the mean of n observations is $1/\sqrt{n}$ of the error in a single observation.

An example of EVOP is shown in Fig. II-41 as applied to a chemical process with two independent variables, reaction temperature t and feed rate V. Three dependent variables were optimized, namely yield A, throughput B, and coast C. Each cycle was a full two-level factorial experiment for two variables (2^2 design) with a non-replicated centre point. The values of the dependent variables obtained during the first phase comprising four cycles are shown in Fig. II-41*a*, *b* and *c*. Figure II-41*a* shows A as a function of t and V. Figure II-41*b* relates B to t and V. Figure II-41*c* relates C to t

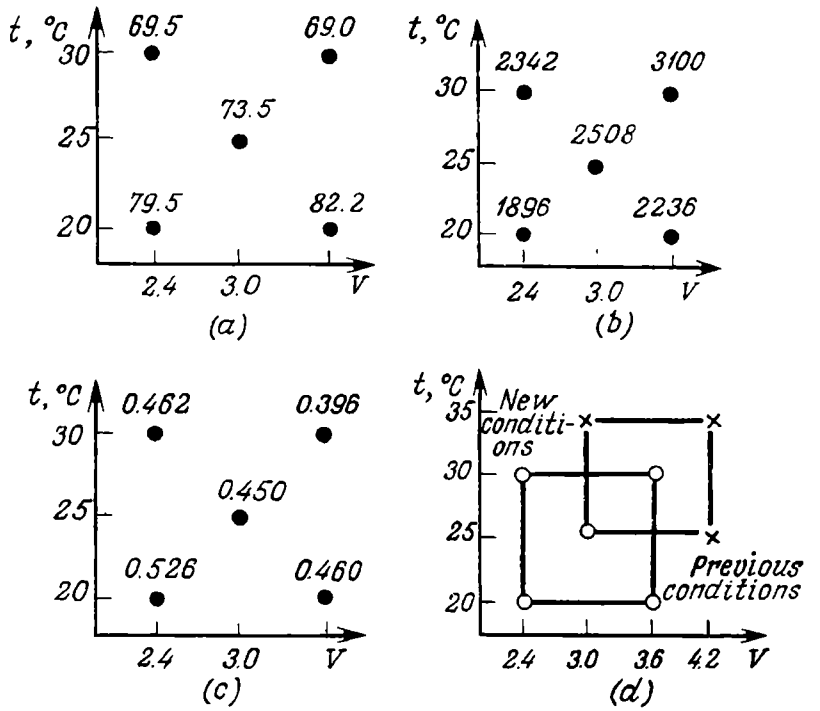


Fig. II-41. Graphical representation of EVOP (the first three graphs represent the results of experiments in the first phase)

(*a*) product yield, %; (*b*) throughput per day; (*c*) cost per unit of product; (*d*) design for the second phase

and V. It was found that the optimum conditions in terms of cost ($t = 30°C$ and $V = 3.6$) were not such in terms of yield ($t = 20°C$, $V = 3.6$).

Figure II-41*d* shows the experimental design for the second phase in which the point of an optimum cost in the first phase was chosen as the centre. As a rule, the centre of the design for every next phase is the point yielding the best response in the previous phase.

At the end of each phase, the experimenter has a choice of three alternatives: (a) to move to a new centre and, as a consequence, to shift the entire experimental region; (b) to change the increments in the independent variables; or (c) to leave the previous independent variables at the optimum level achieved and select new ones.

A measure of how close the optimum has been approached (a measure of the curvature of the response surface) is given by the "change in mean" calculated as the difference between the grand mean for all the observations and the values for the centre of the design, y_0:

$$\frac{y_1+y_2+y_3+y_4+y_0}{5} - y_0 = \frac{y_1+y_2+y_3+y_4+4y_0}{5}$$

If the "change in mean" is positive, the response surface is concave, and experiments are conducted near the minimum. If the "change in mean" is negative, the response surface is convex (hill-like), and experiments are conducted near the maximum.

In the example of Fig. II-41, the "change in mean" appears to be small for all dependent variables. This is an indication that experiments were conducted far away from the extremum.

The application of EVOP to chemistry and chemical engineering is discussed in a number of publications.[35-37]

Example II-13. We seek to determine how the solubility of sodium thiosulphate, y, depends on temperature, x. The sample size is $N = 9$. Experimental data are collected in Table II-20.

Table II-20

x (°C)	0	10	20	30	40	50	60	70	80
y (%)	33.5	37.0	41.2	4.61	50.0	52.0	56.3	64.3	69.9

Solution. The estimated regression equation has the form

$$\hat{y} = b_0 + b_1 x$$

The b_1 coefficient can be found by Eq. (II-154), and the b_0 coefficient by Eq. (II-155). For this purpose, the experimental data and the calculation results should be tabulated as shown in Table II-21.

Table II-21

N	x	y	x^2	xy	y^2	$x+y$	$(x+y)^2$
1	0	33.5	0	0	1122.25	33.5	1122.25
2	10	37.0	100	370	1369.00	47.0	2209.00
3	20	41.2	400	824	1697.44	61.2	3745.44
4	30	46.1	900	1383	2125.21	76.1	5791.21
5	40	50.0	1000	2000	2500.00	90.0	8100.00
6	50	52.8	2500	2645	2798.1	102.9	10,588.41
7	60	56.8	3600	3408	2226.24	116.8	13,642.24
8	70	64.3	4900	4501	4134.49	134.3	18,036.49
9	80	69.9	6400	5592	4886.01	149.9	22,470.01
$\sum$	300	451.7	20,400	20,723	23,859.05		85,705.05

The last two columns in Table II-21 are used only for a check by the following equation:

$$\sum_{i=1}^{N} (x_i+y_i)^2 = \sum_{i=1}^{N} x_i^2 + 2\sum_{i=1}^{N} x_i y_i + \sum_{i=1}^{N} y_i^2$$

In our case,

$$87{,}705.05 = 20{,}400+2\times20{,}723+23{,}859.05$$

which shows that the calculations have been correct.

Using the data of Table II-21, find b_0 and b_1

$$b_1 = \frac{9\times20{,}723-360\times451.7}{9\times20{,}400-360^2} = 0.44$$

$$b_0 = \frac{451.7-0.44\times360}{9} = \frac{293.3}{9} = 32.6$$

Find the sample correlation coefficient by Eq. (II-157):

$$r^* = 0.44\sqrt{\frac{9\times20{,}400-360^2}{9\times23{,}859.05-451.7^2}} = 0.44\sqrt{\frac{54{,}000}{10{,}699}} = 0.99$$

The sample correlation coefficient is very close to unity. This implies that the relation between y and x is practically linear and has the form

$$\hat{y} = 32.6+0.44x$$

Example II-14.[38] We seek to determine how the degree of extraction of sulphuric acid, y, from pickling liquor depends on the original concentration of sulphuric acid x_1, the concentration of ferrous oxide sulphate x_2, and the volumetric ratio of alcohol to acid, x_3. The statistical data have been obtained from a passive experiment, and the sample contains $N = 105$ observations.

Solution. From past plant records it is known that in the region under investigation, the degree of extraction of sulphuric acid is a linear function of the selected factors. Therefore, we describe this functional relationship by an estimated linear regression equation of the form

$$\hat{y} = b_0+b_1x_1+b_2x_2+b_3x_3$$

which we will test for adequacy by the multiple correlation method. Using Eqs. (II-178), we convert all experimental data to a standard scale. Then, on the basis of Eq. (II-180), we find the sample correlation coefficients

$$r^*_{yx_1} = 0.212 \qquad r^*_{x_1x_2} = -0.417$$
$$r^*_{yx_2} = 0.043 \qquad r^*_{x_1x_3} = -0.128$$
$$r^*_{yx_3} = 0.903 \qquad r^*_{x_2x_3} = 0.046$$

Substituting the sample correlation coefficients in Eqs. (II-184), we get

$$\left.\begin{aligned} a_1-0.417a_2-0.128a_3 &= 0.212 \\ -0.417a_1+a_2+0.046a_3 &= 0.043 \\ -0.128a_1+0.046a_2+a_3 &= 0.903 \end{aligned}\right\} \qquad (a)$$

On solving Eqs. (a), we find:

$$a_1 = 0.397, \quad a_2 = 0.166, \quad a_3 = 0.903$$

Then, converted to the standard scale, the estimated regression equation will be

$$\hat{y}^0 = 0.397x_1^0 + 0.166x_2^0 + 0.903x_3^0$$

Using Eqs. (II-188), we switch back to the natural scale:

$$\hat{y} = -26.5 + 1.987x_1 + 1.17x_2 + 14.14x_3$$

Now we apply the Fisher F-test to determine the adequacy of the above equation:

$$F = s_r^2/s_e^2$$

The error mean square, s_e^2, can be found from three replicate observations

$$s_e^2 = \frac{\sum_{i=1}^{3} (y_i - \bar{y})^2}{2} = 3.82$$

where $\bar{y}$ is the mean of the replicate observations. The number of degrees of freedom for s_e^2 is two. The residual mean square, s_r^2, can be found by Eq. (II-170):

$$s_r^2 = \frac{\sum_{i=1}^{105} (y_i - \hat{y}_i)^2}{105 - 4} = 36.03$$

The number of degrees of freedom for the residual mean square is 101. The Fisher variance ratio is, thus, 9.4. The tabulated value of the variance ratio for a significance level of $p = 0.05$ and $f_1 = 101$ and $f_2 = 2$ degrees of freedom is $F_p(f_1, f_2) = 19.5$.[23] Thus, the estimated regression equation fits the experimental data adequately.

Example II-15. We seek the functional relationship between the throughput of a tubular reactor in the manufacture of polyethylene, y, and the process variables[39] (Fig. II-42). The factors to be studied are: the reactor pressure, x_1; the reactor temperature, x_2; the O_2 concentration of the stock, x_3; and the flow rate of the gas fed into the reactor, x_4. The sample size is 200 observations collected under normal operating conditions.

Solution. According to Eq. (II-208), the functional relationship we are seeking can be fitted by an estimated regression equation of the form

$$\hat{y} = af_1(x_1)f_2(x_2)f_3(x_3)f_4(x_4)$$

The unknown functions $f(x)$ and the a coefficient will be estimated by Brandon's method. To begin with, we plot the throughput y as a function of pressure x_1 on the basis of the experimental data (Fig. II-42*a*). The empirical regression line shows that the function $f_1(x_1)$ should preferably be sought as a second-order parabola

$$f_1(x_1) = b_0 + b_1x_1 + b_{11}x_1^2$$

After estimating b_0, b_1 and b_{11} by the least squares method, Eq. (II-172), we get:

$$f_1(x_1) = -211 + 0.33x_1 - 1.16 \times 10^{-4}x_1^2$$

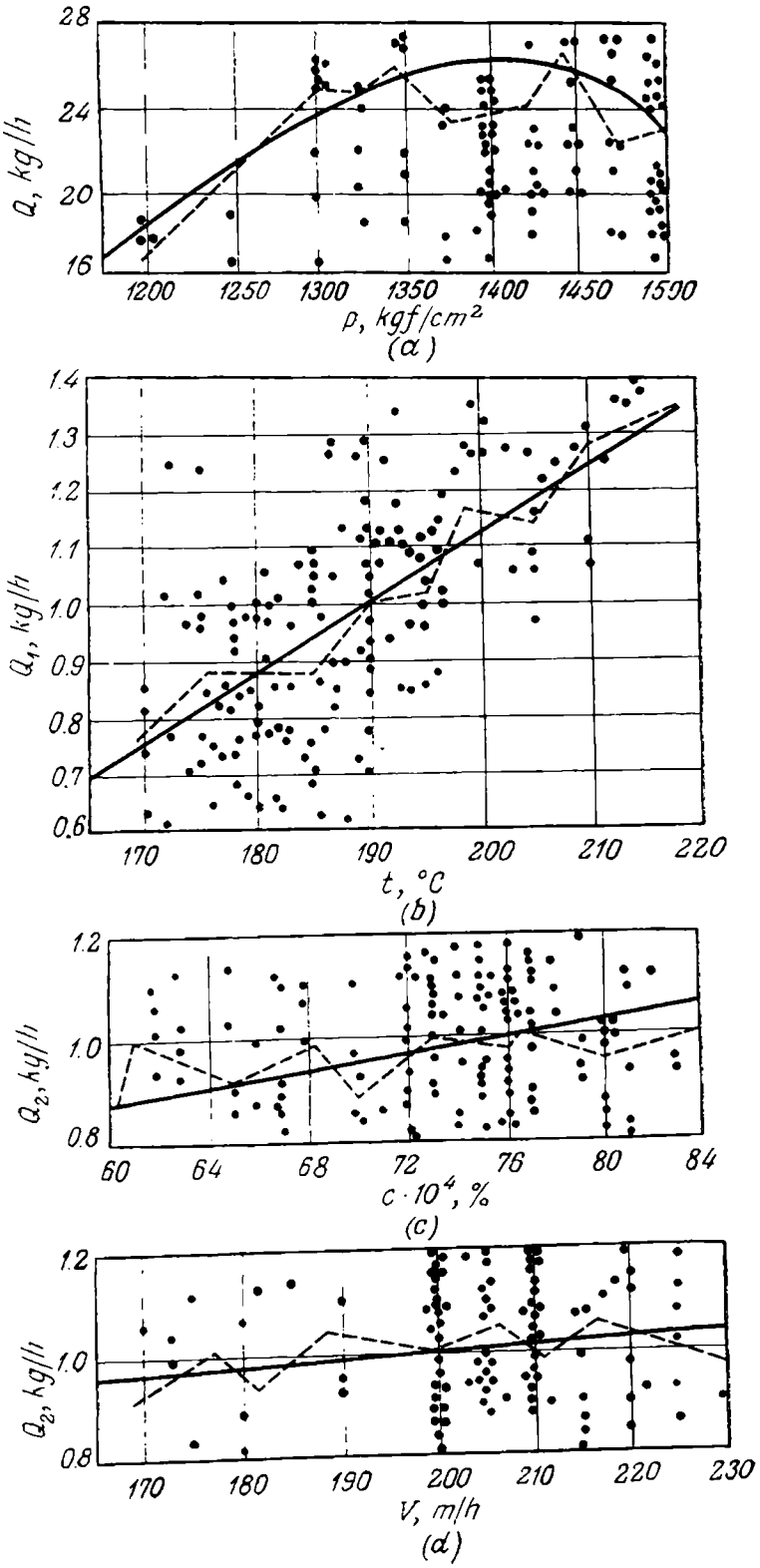


Fig. II-42. To Example II-15

Then, using Eq. (II-209), we form the sample of y_1, construct a correlation field and an empirical regression line, $y_1 - x_2$ (Fig. II-42*b*). An adequate fit is obtained with a linear regression equation of the form

$$\hat{y}_{x_2} = f_2(x_2) = -1.46 + 0.013x_2$$

Proceeding in a similar way with the remaining two factors (Fig. II-42*c* and *d*), we finally obtain the functional relationship between the throughput and process variables:

$$\hat{y} = 1.02(-211 + 0.33x_1 - 1.16 \times 10^{-4} x_1^2)(0.013x_2 - 1.46)(0.0077x_3 + 0.42) \times (0.00127x_4 + 0.747)$$

Example II-16.[40] We seek the conditions that maximize the decomposition of borates by a mixture of sulphuric and phosphoric acids. The factors controlling the degree of decomposition, y, are chosen to be: z_1, the reaction temperature in °C; z_2, the reaction time in minutes; z_3, the norm of phosphoric acid in %; and z_4, the concentration of phosphoric acid in terms of % P_2O_5.

The principal level and the incremental changes in the factors are listed in Table II-22.

Table II-22

	z_1	z_2	z_3	z_4
z_j^0	55	37.5	80	32.8
Δz_j	25	22.5	20	18.8

Solution. From the previous experiments it is known that the optimum process conditions lie within the range of changes in the factors under study (see Table II-22). Therefore, we shall use a second-order orthogonal design in deriving an estimated regression equation (Table II-23). The number of observations in the design matrix for $k = 4$ is 25. The star arm is $\alpha = 1.41$ (see Table II-16). The natural variables z are transformed into dimensionless variables x by Eq. (II-216).

The error mean square is found from four repeated observations at the centre point of the design ($y_1^0 = 61.8\%$, $y_2^0 = 59.3\%$, $y_3^0 = 58.7\%$, $y_4^0 = 69\%$):

$$\bar{y}^0 = \frac{\sum_{i=1}^{4} y_i^0}{4} = 60.95$$

$$s_e^2 = \frac{\sum_{i=1}^{4} (y_i^0 - \bar{y}^0)^2}{3} = 5.95$$

Table II-23

No.	x_0	x_1	x_2	x_3	x_4	x_1'	x_2'	x_3'	x_4'	x_1x_2	x_1x_3	x_1x_4	x_2x_3	x_2x_4	x_3x_4	y
1	+1	+1	+1	+1	+1	0.2	0.2	0.2	0.2	+1	+1	+1	+1	+1	+1	86.9
2	+1	−1	−1	+1	+1	0.2	0.2	0.2	0.2	+1	−1	−1	−1	−1	+1	40.0
3	+1	+1	−1	−1	+1	0.2	0.2	0.2	0.2	−1	−1	+1	+1	−1	−1	66.0
4	+1	−1	+1	−1	+1	0.2	0.2	0.2	0.2	−1	+1	−1	−1	+1	−1	34.4
5	+1	+1	−1	+1	−1	0.2	0.2	0.2	0.2	−1	+1	−1	−1	+1	−1	76.6
6	+1	−1	+1	+1	−1	0.2	0.2	0.2	0.2	−1	−1	+1	+1	−1	−1	55.7
7	+1	+1	+1	−1	−1	0.2	0.2	0.2	0.2	+1	−1	−1	−1	−1	+1	91.0
8	+1	−1	−1	−1	−1	0.2	0.2	0.2	0.2	+1	+1	+1	+1	+1	+1	47.6
9	+1	+1	−1	+1	+1	0.2	0.2	0.2	0.2	−1	+1	+1	−1	−1	+1	74.1
10	+1	−1	+1	+1	+1	0.2	0.2	0.2	0.2	−1	−1	−1	+1	+1	+1	52.0
11	+1	+1	+1	−1	+1	0.2	0.2	0.2	0.2	+1	−1	+1	−1	+1	−1	74.5
12	+1	−1	−1	−1	+1	0.2	0.2	0.2	0.2	+1	+1	−1	+1	−1	−1	29.6
13	+1	+1	+1	+1	−1	0.2	0.2	0.2	0.2	+1	+1	−1	+1	−1	−1	94.8
14	+1	−1	−1	+1	−1	0.2	0.2	0.2	0.2	+1	−1	+1	−1	+1	−1	49.6
15	+1	+1	−1	−1	−1	0.2	0.2	0.2	0.2	−1	−1	−1	+1	+1	+1	68.6
16	+1	−1	+1	−1	−1	0.2	0.2	0.2	0.2	−1	+1	+1	−1	−1	+1	51.8
17	+1	0	0	0	0	−0.8	−0.8	−0.8	−0.8	0	0	0	0	0	0	61.8
18	+1	+1.414	0	0	0	1.2	−0.8	−0.8	−0.8	0	0	0	0	0	0	95.4
19	+1	−1.414	0	0	0	1.2	−0.8	−0.8	−0.8	0	0	0	0	0	0	41.7
20	+1	0	+1.414	0	0	−0.8	1.2	−0.8	−0.8	0	0	0	0	0	0	79.0
21	+1	0	−1.414	0	0	−0.8	1.2	−0.8	−0.8	0	0	0	0	0	0	42.4
22	+1	0	0	+1.414	0	−0.8	−0.8	1.2	−0.8	0	0	0	0	0	0	77.6
23	+1	0	0	−1.414	0	−0.8	−0.8	1.2	−0.8	0	0	0	0	0	0	58.0
24	+1	0	0	0	+1.414	−0.8	−0.8	0.8	1.2	0	0	0	0	0	0	45.6
25	+1	0	0	0	−1.414	−0.8	−0.8	0.8	1.2	0	0	0	0	0	0	52.3

The number of degrees of freedom for the error mean square is $f = 4 - 1 = 3$.

Using Eqs. (II-243 and II-244) we estimate the cofficients of the second-order regression equation and the standard errors of estimate of these coefficients.

$$b_0 = 61.54 \qquad b_{44} = -5.34 \qquad s_{b_j} = \sqrt{s_{b_j}^2} = 0.545$$

$$b_1 = 17.37 \qquad b_{12} = 2.18 \qquad s_{b_{uj}} = \sqrt{s_{b_{uj}}^2} = 0.61$$

$$b_{13} = 0.2$$

$$b_2 = 6.4 \qquad b_{14} = 1.2 \qquad s_{b_{jj}} = \sqrt{s_{b_{jj}}^2} = 0.864$$

$$b_3 = 4.7 \qquad b_{23} = 0.56$$

$$b_4 = -4.37 \qquad b_{24} = 0.79$$

$$b_{11} = 4.5 \qquad b_{34} = 1_n$$

$$b_{22} = 1.3$$

$$b_{33} = 4.09$$

The significance of the coefficients is tested with the Student t-test, see Eq. (II-165):

$$t_1 = \frac{17.37}{0.545} = 31.9 \qquad t_{12} = \frac{2.18}{0.61} = 3.57$$

$$t_2 = \frac{6.4}{0.545} = 11.7 \qquad t_{34} = \frac{1.9}{0.61} = 3.8$$

$$t_3 = \frac{4.70}{0.545} = 8.64 \qquad t_{13} = \frac{0.2}{0.61} = 3.18$$

$$t_4 = \frac{4.37}{0.545} = 8.04 \qquad t_{14} = \frac{1.2}{0.61} = 1.97$$

$$t_{11} = \frac{4.5}{0.864} = 5.2 \qquad t_{23} = \frac{0.56}{0.61} = 0.91$$

$$t_{22} = \frac{1.3}{0.864} = 1.5 \qquad t_{24} = \frac{0.76}{0.61} = 1.25$$

$$t_{33} = \frac{4.09}{0.864} = 4.73$$

$$t_{44} = \frac{5.34}{0.864} = 6.22$$

The tabulated value of the Student t^{23} for a significance level of $p = 0.05$ and $f = 3$ degrees of freedom is $t_p(f) = 3.18$.

After dropping the insignificant coefficients for which the t-ratio is less than the tabulated value, we obtain the estimated regression equation in dimensional form:

$$\hat{y} = 61.54+17.37x_1+6.4x_2+4.7x_3-4.37x_4+2.18x_1x_2+1.9x_3x_4 +4.5(x_1^2-0.8)+4.09(x_3^2-0.8)-5.34(x_4^2-0.8) = 58.9+17.37x_1 +6.4x_2+4.7x_3-4.37x_4+2.18x_1x_2+1.9x_3x_4+4.5x_1^2 +4.09x_3^2-5.34x_4^2$$

To test the estimated regression equation for the adequacy of fit, we determine the residual mean square

$$s_r^2 = \frac{\sum_{i=1}^{N}(y_i-\hat{y}_i)^2}{N-l} = \frac{396.2}{25-10} = 26.4$$

and find the F (variance) ratio:

$$F = s_r^2/s_e^2 = 26.4 \div 5.95 = 4.4$$

The tabulated value of the Fisher F for a significance level of $p = 0.05$ and $f_1 = 15$ and $f_2 = 3$ degrees of freedom is 8.6. Thus, $F < F_p(f_1, f_2)$, and the estimated regression equation fits the experimental data adequately.

On the natural scale, the estimated regression equation, Eq. (II-216), takes the form

$$\hat{y} = 90.64-0.242z_1-0.07z_3+0.35z_4+0.00388z_1z_2 +0.00506z_3z_4+0.0072z_1^2+0.0102z_3^2-0.015z_4^2$$

The conditions answering $\hat{y} = 100\%$ as found from the last regression equation by the Gauss-Seidell method on a MINSK-22 computer were: $z_1 = 90°C$, $z_2 = 50$ min, $z_3 = 90\%$, and $z_4 = 32.5$.

Under the optimum conditions thus obtained, check experiments were conducted. The borates were found to have been decomposed 98.5% by thermal phosphoric acid with a concentration of 30.3% P_2O_5, and 98.9% by wet-process phosphoric acid with a concentration of 29.6% P_2O_5.

Example II-17.[41] We seek the functional relationship between the impurities in wet-process phosphoric acid and the degree of decomposition, y, of the flotation concentrate of phosphorite and also the conditions that will maximize the degree of decomposition, y_{max}. The factors governing the decomposition are chosen to be: z_1, the process temperature in °C; z_2 through z_5, the MgO, SO_3, Al_2O_3 and F contents (by weight per cent) of phosphoric acid, respectively.

The principal level, incremental changes, and the boundaries of the feasible region are listed in Table II-24.

The range of changes in the factors (see Table II-24) corresponds to the range of impurity contents of commercial phosphoric acid. Therefore, no

Table II-24

	z_1	z_2	z_3	z_4	z_5
z_j^0	50	2.1	2.0	1.33	0.75
Δz_j	20	0.9	1.0	0.37	0.25
+2	90	3.9	4.0	2.07	1.25
−2	10	0.3	0.0	0.59	0.25

extrapolation beyond the limits stated in Table II-24 is needed in determining y_{max}.

Solution. A second-order rotatable design will be used to derive an estimated regression equation (see Table II-25).

The number of observations in the design matrix for $k = 5$ is 32. The kernel of the design is a half-replicate of a 2^{5-1} design with a generating relation $x_5 = x_1x_2x_3x_4$. The star arm $\alpha = 2$ and $n_0 = 6$ are found from Table II-18. The natural variables z's are transformed into dimensionless variables x's by Eq. (II-216).

The error mean square as found from the observations at the centre point of the design is:

$$s_e^2 = 4.466$$

for which the number of degrees of freedom is $f = n_0 - 1 = 5$.

Using Table II-25 and Eqs. (II-250) through (II-257), we estimate the coefficients of the second-order regression equation and their standard errors of estimate

$b_0 = 34.41$ $b_{12} = 0.147$ $s_{b_j} = \sqrt{s_{b_j}^2} = 0.43$

$b_1 = 1.07794$ $b_{13} = 0.256$ $s_{u_j} = \sqrt{s_{u_j}^2} = 0.53$

$b_2 = -0.146$ $b_{14} = 1.61$ $s_{b_{jj}} = \sqrt{s_{b_{jj}}^2} = 0.394$

$b_3 = 4.5098$ $b_{15} = 0.0534$

$b_4 = -0.542$ $b_{23} = 0.736$

$b_5 = -1.3$ $b_{24} = -0.198$

$b_{11} = -1.5$ $b_{25} = 0.403$

$b_{22} = 2.66$ $b_{34} = 0.401$

$b_{33} = -1.47$ $b_{35} = 0.256$

$b_{44} = -0.93$ $b_{45} = 0.93$

$b_{55} = -0.15$

Table II-25

	x_1	x_2	x_3	x_4	x_5	y
1	+1	+1	+1	+1	+1	34.7
2	−1	+1	+1	+1	−1	40
3	+1	−1	+1	+1	−1	39.0
4	−1	−1	+1	+1	+1	39.2
5	+1	+1	−1	+1	−1	26.6
6	−1	+1	−1	+1	+1	29.5
7	+1	−1	−1	+1	+1	30.0
8	−1	−1	−1	+1	−1	34.5
9	+1	+1	+1	−1	−1	32.2
10	−1	+1	+1	−1	+1	41.4
11	+1	−1	+1	−1	+1	33.7
12	−1	−1	+1	−1	−1	40.9
13	+1	+1	−1	−1	+1	23.9
14	−1	+1	−1	−1	−1	33.3
15	+1	−1	−1	−1	−1	27.7
16	−1	−1	−1	−1	+1	35.9
17	−2	0	0	0	0	25
18	+2	0	0	0	0	33.3
19	0	−2	0	0	0	49.2
20	0	+2	0	0	0	42.0
21	0	0	−2	0	0	17.5
22	0	0	+2	0	0	41.0
23	0	0	0	−2	0	35.6
24	0	0	0	+2	0	27.2
25	0	0	0	0	−2	39.0
26	0	0	0	0	+2	30.0
27	0	0	0	0	0	35.4
28	0	0	0	0	0	36.4
29	0	0	0	0	0	33.2
30	0	0	0	0	0	32.4
31	0	0	0	0	0	37.7
32	0	0	0	0	0	36.9

The significance of the coefficients is tested, using the Student t-test (Eq. II-165):

$$t_1 = \frac{1.07}{0.33} = 2.48 \qquad t_{12} = \frac{0.147}{0.53} = 0.278$$

$$t_2 = \frac{0.146}{0.43} = 0.34 \qquad t_{13} = \frac{0.256}{0.53} = 0.483$$

$$t_3 = \frac{4.51}{0.43} = 10.4 \qquad t_{14} = \frac{1.61}{0.53} = 3.04$$

$$t_5 = \frac{1.3}{0.43} = 3.02 \qquad t_{15} = \frac{0.0534}{0.53} = 0.1$$

$$t_{11} = \frac{1.5}{0.394} = 3.82 \qquad t_{23} = \frac{0.736}{9.53} = 0.1375$$

$$t_{22} = \frac{2.66}{0.394} = 6.75 \qquad t_{24} = \frac{0.198}{0.53} = 0.374$$

$$t_{33} = \frac{1.47}{0.394} = 3.73 \qquad t_{25} = \frac{0.403}{0.53} = 0.762$$

$$t_{44} = \frac{0.93}{0.394} = 2.36 \qquad t_{34} = \frac{0.401}{0.53} = 0.758$$

$$t_{55} = \frac{0.15}{0.394} = 0.38 \qquad t_{45} = \frac{0.93}{0.53} = 1.75$$

For a significance level of $p = 0.05$ and $f = 5$ degrees of freedom, the tabulated value of the t-ratio is $t_p(f) = 2.57$. After the coefficients for which the t-ratio is smaller than the tabulated value are dropped, the estimated regression equation in dimensionless form becomes:

$$\hat{y} = 35.4 + 4.51x_3 - 1.3x_5 - 1.5x_1^2 + 2.66x_2^2 - 1.47x_3^2 + 1.61x_1x_4$$

The Fisher F-test shows that the above equation fits the data adequately:

$$s_e^2 = 4.466 \qquad s_r^2 = 15.35 \qquad F = 3.43$$

$$F_{p=0.05}(25.5) = 4.5$$

Converted back to the natural scale, the equation takes the form

$$\hat{y} = 44.04 + 0.086z_1 - 13.8z_2 + 10.39z_3 - 10.9z_4 - 5.2z_5 - 0.00375z_1^2 + 3.28z_2^2 - 1.4z_3^2 + 0.217z_1z_4$$

The above equation gives an idea about the degrees of decomposition of the stock at different temperatures, depending on the impurity content of the acid. To find the conditions which lead to the maximum value of decomposition, y_{max}, the significant factors are set constant: $x_2 = +2$ and $x_5 = -2$.

The effect of the SO_3 content of phosphoric acid is represented by a positive linear and a negative quadratic term. The optimum SO_3 content of 1.533% is found from the value of y maximized by x_3. Then the estimated regression equation takes the form

$$\hat{y} = 52.12 - 1.5x_1^2 + 1.61x_1x_4$$

To determine the optimum temperature, x_1, and the optimum Al_2O_3 content, x_4, we transform the last equation to its canonical form:

$$\hat{y} - 52.12 = 0.35X_1^2 - 1.85X_4^2$$

where 52.12 is the degree of decomposition at the centre point, S, of the response surface.

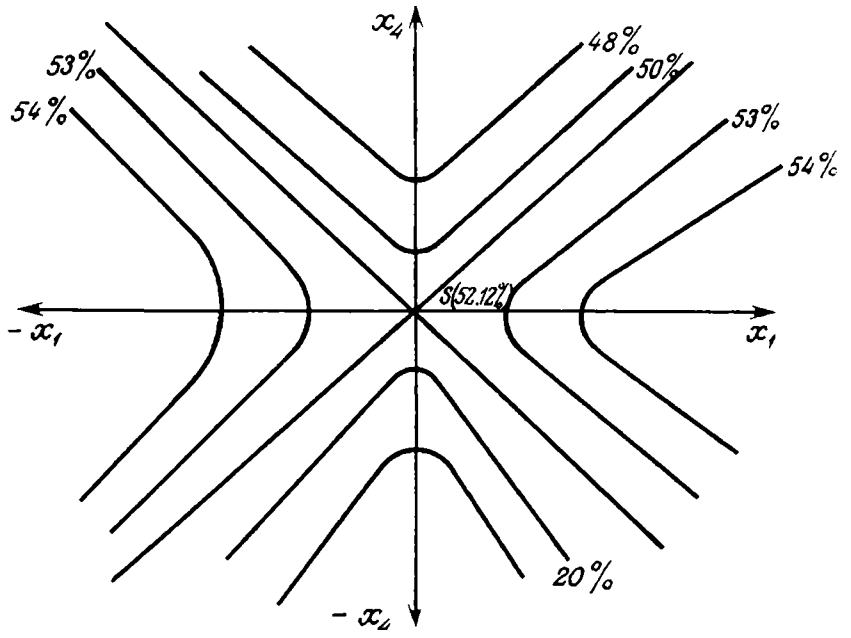


Fig. II-43. To Example II-17

The response surface is a hyperbolic paraboloid. Planes of constant value, $y = \text{const}$, passing through the response surface produce hyperbolas (Fig. II-43). The centre is a minimax (saddle) point. X can be transformed back to x, using the equations:[42]

$$x_1 = (X_1 + x_{1S}) \cos \varphi - (X_4 + X_{4S}) \sin \varphi$$

$$x_4 = (X_1 + x_{1S}) \sin \varphi + (X_4 + x_{4S}) \cos \varphi$$

$$\tan 2\varphi = \frac{b_{14}}{b_{11} - b_{44}}$$

To find the maximum degree of decomposition, we start out from the minimax (saddle) point along the x_1 axis (the canonical coefficient is positive), by equating x_4 to zero:

$$x_1 = \pm \sqrt{\frac{\hat{y} - 52.12}{0.35}} \qquad x_4 = 0$$

While incrementing $\hat{y}$, we check to see if the condition $x_1 = x_4 \leqslant 2$ is satisfied. The maximum degree of decomposition is found to be 53.5% ($x_1 = \pm 1.82$, $x_4 = \pm 0.795$). With y raised to 54%, $x_1 > 2$. Check tests run under the optimum conditions thus obtained ($x_1 = +1.82$, $x_2 = +2$, $x_3 = +1.533$, $x_4 = +0.795$, $x_5 = -2$ and $x_1 = -1.82$, $x_2 = +2$, $x_3 = +1.533$, $x_4 = -0.795$ and $x_5 = -2$) yielded a decomposition of 55.8% and 53.7%, respectively. Thus, the discrepancy between the calculated data ($\hat{y} = 53.5\%$) and the experimental data ($\bar{y} = 54.7\%$) is within the limits of experimental error ($s_y = \sqrt{4.466} = 2.1$).

Example II-18.[33] A reaction proceeding according to the scheme $A+B+C \rightarrow D$ in a water-alcohol solution was investigated. The quality and quantity of the reaction product, $D(y)$, were governed by the reaction time in hours, z_1; the alcohol content of the solution in mole fractions, z_2; the C content of the stock in mole fractions, z_3; the D content of the stock in mole fractions, z_4; and the ratio B/A, z_5. The principal level and the incremental changes are listed in Table II-26.

Table II-26

	z_1	z_2	z_3	z_4	z_5
z_j^0	2.0	0.65	0.10	0.25	1.20
Δz_j	0.20	0.15	0.025	0.05	0.20

We seek to find the set of operating conditions which maximize the yield of the D product, $D(y_{max})$.

Solution. We shall use a regular simplex design. From matrix X (see II-267), we select a submatrix containing five columns and six rows (or $k = 5$ and $N = k+1$). Using the coding equation, Eq. (II-216), we get

$$x_1 = \frac{z_1 - 2.0}{0.20} \qquad x_3 = \frac{z_3 - 0.10}{0.10}$$

$$x_2 = \frac{z_2 - 0.65}{0.15} \qquad x_4 = \frac{z_4 - 0.25}{0.05}$$

$$x_5 = \frac{z_5 - 1.20}{0.20}$$

Then the matrix of the original simplex on the natural scale will have the form given in Table II-27.

Table II-27

N	z_1	z_2	z_3	z_4	z_5	y
1	2.10	0.693	0.105	0.258	1.225	0.760
2	1.90	0.693	0.105	0.258	1.225	0.491
3	2.00	0.564	0.105	0.258	1.225	0.513
4	2.00	0.650	0.085	0.258	1.225	0.675
5	2.00	0.650	0.100	0.218	1.225	0.693
6	2.00	0.650	0.100	0.250	1.075	0.666

As is seen from the above table, the poorest response is obtained at vertex 2. We replace this vertex with its mirror reflection, vertex 7. The coor-

dinates of the added vertex are found by Eqs. (II-268) and (II-269). To begin with, we find the coordinates of point C, the centre of the face formed by vertices 1, 3, 4, 5 and 6:

$$z_1^{(c)} = \frac{4\times 2.00+2.1}{5} = 2.02$$

$$z_2^{(c)} = \frac{3\times 0.65+0.504+0.693}{5} = 0.641$$

$$z_3^{(c)} = \frac{2\times 0.105+0.085+20.100}{5} = 0.099$$

$$z_4^{(c)} = \frac{3\times 0.258+0.218+0.250}{5} = 0.298$$

$$z_5^{(c)} = \frac{4\times 1.225+1.075}{5} = 1.195$$

Then the coordinates of the added, seventh, vertex will be

$$z_1^{(7)} = 2\times 2.02-1.90 = 2.14$$

$$z_2^{(7)} = 2\times 0.641-0.693 = 0.589$$

$$z_3^{(7)} = 2\times 0.099-0.105 = 0.093$$

$$z_4^{(7)} = 2\times 0.248-0.258 = 0.238$$

$$z_5^{(7)} = 2\times 1.195-1.225 = 1.165$$

The added, seventh, vertex and the remaining vertices 1, 3, 4, 5 and 6 form a new regular simplex (Table II-28).

Table II-28

N	z_1	z_2	z_3	z_4	z_6	y
1	2.10	0.693	0.105	0.258	1.225	0.760
3	2.00	0.569	0.105	0.258	1.225	0.513
4	2.00	0.650	0.085	0.258	1.225	0.675
5	2.00	0.650	0.100	0.218	1.225	0.693
6	2.00	0.650	0.100	0.250	1.075	0.666
7	2.14	0.589	0.093	0.238	1.165	0.810

After an experiment with its centre at vertex 7, the poorest response was obtained at vertex 3. Its reflection from face 1-4-5-6-7 defines the centre for the next design, etc. After the seventh experiment, one more factor, z_6, the speed of the agitator, was added. Until then, z_6, had been held constant, $z_6^0 = 800$ min^{-1}. The coordinates of the 8th vertex in dimensionless form are

$$x_1^{(0)}, x_2^{(0)}, \ldots, x_{k+1}^{(0)}+h_{k+1}$$

The unit of incremental change is $\Delta z_6 = 100$ min $^{-1}$, and the principal level is $z_6^0 = 800$ min $^{-1}$. Then the coding equation for z_6 has the form

$$x_6 = \frac{z_6 - 800}{100} \qquad x_6^0 = 0$$

The height of the six-dimensional simplex is found by Eq. (II-263) to be $h_6 = 0.764$. Now we shall find the set of factors for experiment No.8. The first five factors are the coordinates of the centroid of five-dimensional simplex 1-3-4-5-6-7 (see Table II-28):

$$z_1^{(0)} = z_1^{(8)} = \frac{2.10 + 4 \times 2.0 + 2.14}{6} = 2.04$$

$$z_2^{(0)} = z_2^{(8)} = 0.633$$

$$z_3^{(0)} = z_2^{(8)} = 0.098$$

$$z_4^{(0)} = z_4^{(8)} = 0.247$$

$$z_5^{(0)} = z_5^{(8)} = 1.19$$

$$z_6^{(8)} = 800 + 100x_6^{(8)} = 800 + 100(x_6^0 + h_6) = 877 \text{ min}^{-1}$$

Vertex 8 together with vertices 1, 3, 4, 5, 6 and 7 form a six-dimensional simplex, 1-3-4-5-6-7 (see Table II-29).

Table II-29

N	z_1	z_2	z_3	z_4	z_5	z_6	y
1	2.10	0.693	0.105	0.258	1.225	800	0.760
3	2.00	0.564	0.105	0.258	1.225	800	0.513
4	2.00	0.650	0.085	0.258	1.225	800	0.675
5	2.00	0.650	0.100	0.218	1.225	800	0.693
6	2.00	0.650	0.100	0.250	1.075	800	0.666
7	2.14	0.589	0.093	0.238	1.165	800	0.810
8	2.04	0.633	0.098	0.247	1.190	877	

After the eighth experiment, the results are evaluated, and the procedure is continued for six factors.

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CHAPTER III

MATHEMATICAL MODELS OF UNIT PROCESSES OF CHEMICAL ENGINEERING

This Chapter will deal with some of the mathematical models for a number of the most common processes and reactors used in chemical engineering. The chemical processes and reactors proper will be examined in a separate chapter (Chap. IV).

III-1. THERMAL PROCESSES

Until quite recently the design of a heat exchanger has been limited to steady-state conditions and to parameters such as average difference in temperature, coefficients of heat transfer, the area of heat transfer, and hydraulic resistance. However, the design of present-day automatically controlled processes and systems makes imperative a knowledge of quantitative relationships in the form of mathematical models which characterize both static (steady-state) and dynamic (unsteady-state) behaviour of heat exchangers.

The following notation will be used in the subsequent discussion:[1]

G_1, G_2 — mass flow rates of heat-transfer media, kg/h

$t_{1\,in}$, $t'_{1\,in}$ — inlet temperature of the hot medium before and after a perturbation, °C

$t_{1\,out}$, $t'_{1\,out}$ — outlet temperature of the hot medium before and after a perturbation, °C

$t_{2\,in}$, $t'_{2\,in}$ — inlet temperature of the cold medium before and after a perturbation, °C

$t_{2\,out}$ $t'_{2\,out}$ — outlet temperature of the cold medium before and after a perturbation, °C

F — heat-transfer surface area, m^2

V — volumetric flow rate of a heat-transfer medium, m^3/h

w — linear velocity of a heat-transfer medium, m/s

c – heat capacity, kcal kg^{-1} deg^{-1} or kcal m^2 deg^{-1}
W_1, W_2 – water equivalents
α – coefficient of heat transfer, kcal m^{-2} h^{-1} deg^{-1}
λ – coefficient of thermal conductivity of a wall, kcal m^{-1} h^{-1} deg^{-1}
l – wall length, m
γ – density, kg/m^3
L – perimeter of a cross-section through a medium, m
φ – angle between cross-current streams
Δp – pressure difference, atm
f_i – cross-sectional area, m^2

The basis of mathematical models is provided by constraint equations which interrelate process (output) variables and controlled and uncontrolled (input) variables. It should be stressed that the heat balance of an exchanger is not a constraint equation because it cannot be used for determining directly the outlet temperature of the exchanger if the inlet temperature of one of the media has been changed. By the same token, one cannot determine this relationship in time, as the exchanger is switched from one set of operating conditions to another.

Model of a steady-state process. Setting constant the flow rates and heat capacities of the media and the coefficient of heat transfer over the heating surface, we may consider two cases.

For a heat exchanger in which one medium (t_2) is under plug-flow conditions and the other medium (t_1) is under perfect-mixing conditions (Fig. III-1), we have:

– with a perturbation applied to $t_{1\,in}$

$$\frac{t_1' - t_{2\,in}}{t_1' - t_{2\,out}'} = \frac{t_1 - t_{2\,in}}{t_1 - t_{2\,out}} \qquad \text{(III-1)}$$

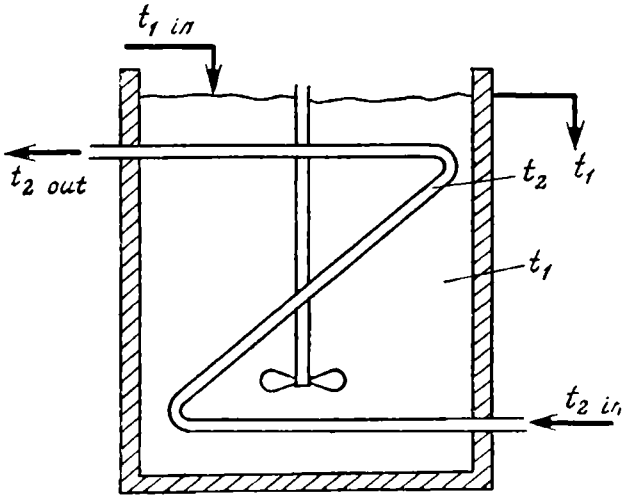


Fig. III-1. Heat exchanger with one fluid in plug flow (t_2) and the other fluid in complete mixing (t_1)

– with a perturbation applied to $t_{2\,in}$

$$\frac{t_1 - t'_{2\,in}}{t_1 - t'_{2\,out}} = \frac{t_1 - t_{2\,in}}{t_1 - t_{2\,out}} \qquad \text{(III-2)}$$

These conditions may be assumed to exist in exchangers where one medium is in the liquid of vapour phase, and also in cases where the velocity and heat capacity of one medium are considerably greater than those of the other.

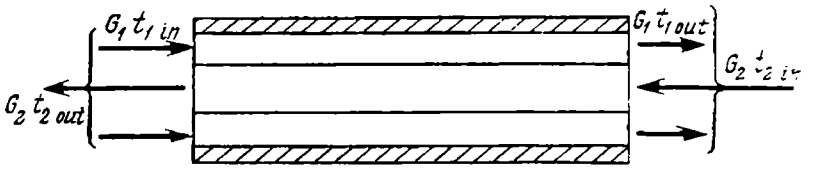


Fig. III-2. Heat exchanger with both fluids in plug flow

For a heat exchanger in which both media are under conditions of plug flow (Fig. III-2), we may write

– with changes in temperature over the $t_{1\,in} \rightarrow t_{1\,out}$ circuit

$$t'_{1\,out} = \frac{(t_{1\,out} - t_{2\,in})(t'_{1\,in} - t_{2\,in})}{t_{1\,in} - t_{2\,in}} - t_{2\,in} \qquad \text{(III-3)}$$

– with changes in temperature over the $t_{2\,in} \rightarrow t_{2\,out}$ circuit

$$t'_{2\,out} = \frac{(t_{2\,out} - t_{2\,in})(t_{1\,in} - t'_{2\,in})}{t_{1\,in} - t_{2\,in}} + t'_{2\,in} \qquad \text{(III-4)}$$

– with changes in temperature over the $t_{1\,in} \rightarrow t_{2\,out}$ circuit

$$t'_{2\,out} = \frac{(t_{2\,out} - t_{2\,in})(t'_{1\,in} - t_{2\,in})}{t_{1\,in} - t_{2\,in}} + t_{2\,in} \qquad \text{(III-5)}$$

– with changes in temperature over the $t_{2\,in} \rightarrow t_{1\,out}$ circuit

$$t'_{1\,out} = \frac{(t_{1\,out} - t_{2\,in})(t_{1\,in} - t'_{2\,in})}{t_{1\,in} - t_{2\,in}} + t'_{2\,in} \qquad \text{(III-6)}$$

The dependence of temperature on position, X, along the exchanger is described by the following equations (assuming a perturbation in t_1 and boundary conditions such that $t_{1\,in} = 1$ and $t_{2\,in} = 0$):

– for cocurrent flow, neglecting the heat capacity of the wall:

$$t_1(X) = \frac{X_4 W_1 + X_1 W_2 e^{w_1 X}}{X_4 W_1 + X_4 W_2} \qquad \text{(III-7)}$$

$$t_2(X) = \frac{W_1 X_4 - W_1 X_4 e^{w_1 X}}{X_4 W_1 + X_1 W_2} \qquad \text{(III-8)}$$

where

$$m = -\frac{W_1X_4 + W_2X_1}{W_1W_2}$$

$$X_1 = \frac{\alpha_1 L_1}{f_1 c_1 \gamma_1} \qquad X_2 = \frac{\alpha_1 L_1}{f_w c_w \gamma_w}$$

$$X_3 = \frac{\alpha_2 L_2}{f_w c_w \gamma_w} \qquad X_4 = \frac{\alpha_2 L_2}{f_2 c_2 \gamma_2}$$

– for countercurrent flow, neglecting the heat capacity of the wall:

$$t_2(X) = \frac{W_1X_4e^{\lambda_2 l} - W_1X_1^{\lambda_2 X}}{W_1X_4e^{\lambda_2 l} - X_1W_2} \tag{III-9}$$

$$t_2(X) = \frac{W_1X_4e^{\lambda_2 l} - W_1X_4^{\lambda_2 X}}{W_1X_4e^{\lambda_2 l} - W_2X_1} \tag{III-10}$$

where

$$\lambda_2 = \frac{X_4}{W_2} - \frac{X_1}{W_1}$$

– for countercurrent flow, with allowance for the heat capacity of the wall:

$$t_1(X) = \frac{W_1\bar{X}_4e^{\lambda l} - W_2\bar{X}_1e^{\lambda X}}{W_1\bar{X}_4e^{\lambda l} - W_2\bar{X}_1} \tag{III-11}$$

$$t_2(X) = \frac{W_1\bar{X}_4e^{\lambda l} - W_1\bar{X}_4e^{\lambda X}}{W_1\bar{X}_4e^{\lambda l} - W_2\bar{X}_1} \tag{III-12}$$

where

$$\bar{X}_1 = \frac{X_1X_3}{X_2+X_3} \qquad \bar{X}_4 = \frac{X_2X_4}{X_2+X_3} \qquad \lambda = \frac{\bar{X}_4}{W_2} - \frac{\bar{X}_1}{W_1}.$$

Model of an unsteady-state process. The basis of this model is the assumption that changes in temperature with position along the exchanger (Fig. III-3) can be linearized. Then the process may be modelled by the following equations (in which Q is the quantity of heat, kcal):

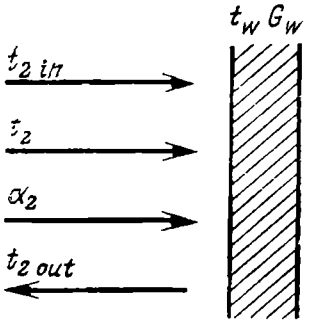


Fig. III-3. Heat transfer through a wall

$$\frac{dQ_1}{d\tau} = \alpha_1 F_1 \left(\frac{t_{1\,in} + t_{1\,out}}{2} - t_w \right) \tag{III-13}$$

$$\frac{dQ_2}{d\tau} = \alpha_2 F_2 \left(t_{w,m} - \frac{t_{2\,in} + t_{2\,out}}{2} \right) \tag{III-14}$$

$$\frac{dQ_1}{d\tau} = V_1 c_1 (t_{1\,in} - t_{1\,out}) \tag{III-15}$$

$$\frac{dQ_2}{d\tau} = V_2 c_2 (t_{2\,out} - t_{2\,in}) \tag{III-16}$$

$$\frac{dQ_1}{d\tau} - \frac{dQ_2}{d\tau} = G_w c_w \frac{dt_w}{d\tau}. \tag{III-17}$$

By solving the above system of simultaneous differential equations, we can determine the manner in which the outlet temperature of the cold medium changes as the inlet temperature of the hot medium is changed stepwise

$$t_{2\,out} = \frac{f}{m}\left(1 - e^{-\frac{m}{r}}\right) \qquad \text{(III-18)}$$

where

$$f = \Delta t_{1\,in} = t_{1\,in} - t_{1\,in}(0)$$

$$m = \frac{V_2 c_2}{\alpha_2 F_2} + \frac{1}{2} + \frac{V_2 c_2 (2V_1 c_1 + \alpha_1 F_1)}{2V_1 c_1 \alpha_1 F_1}$$

$$r = \frac{G_w c_w (2V_1 c_1 + \alpha_1 F_1)}{2V_1 c_1 \alpha_1 F_1}\left(\frac{V_2 c_2}{\alpha_2 F_2} + \frac{1}{2}\right)$$

From Eq. (III-18), we can evaluate the effect of the various parameters on changes in $t_{2\,out}$ while the exchanger is in the design stage, which is important to synthesis of an optimal control system. For example, if we are interested in accelerating the rate of change in $t_{2\,out}$, that is, in minimizing the time lag of a process, we may reduce the weight of the exchanger and calculate the needed relationship in quantitative terms. Besides, Eq. (III-18) gives a clue to the temperature in the new steady state.

With an accuracy sufficient for all practical purposes, the above equations may be applied to heat exchangers for which the inlet to outlet temperature ratio is less than two.

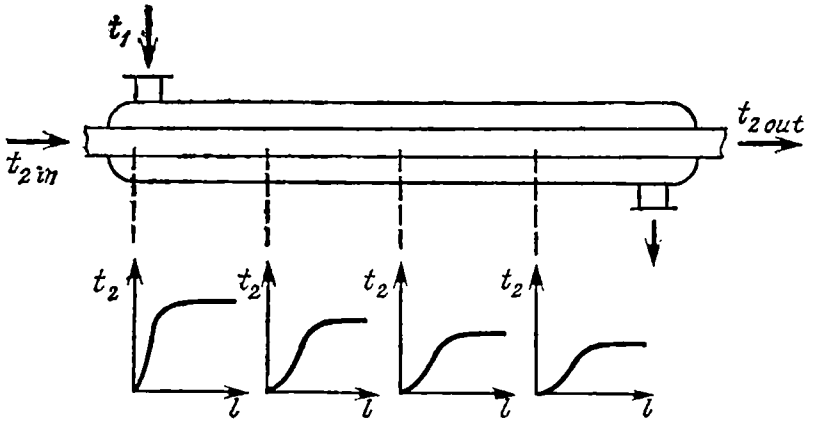


Fig. III-4. Distributed-parameter thermal process

Model of a distributed-parameter process. Studies of unsteady-state processes in heat exchangers have shown that the temperatures of both fluids vary with time and position (Fig. III-4). Such processes are called *distributed-parameter processes*, or simply *distributed processes*. With a considerable degree of parameter distribution, such processes should be described by partial differential equations.

In developing the partial differential equations that model a distributed process, the following assumptions are made:

(a) one of the fluids flows in a straight pipe, and the other in a shell surrounding the pipe;

(b) the fluid is flowing in one direction (in the x-direction);

(c) mixing perpendicular to the direction of flow is complete and so the velocity and temperature at any section normal to the x-axis are averaged;

(d) mixing of the fluids and transfer of heat to the pipe wall in the direction of flow are neglected;

(e) heat capacities and densities of the fluids and wall are deemed constant over the temperature range under consideration;

(f) the coefficients of heat transfer are deemed constant over the entire surface of the heat exchanger;

(g) loss of heat to the surroundings is neglected;

(h) the cross-sectional area and pattern of the flow are deemed constant.

A *model of a heat exchanger under unsteady-state conditions, one fluid being under plug-flow conditions and the other perfectly mixed* (see Fig. III-1). Such a heat exchanger can be modeled by the following equations

$$\left.\begin{aligned} \frac{\partial t_2}{\partial \tau} + \frac{\partial t_2}{\partial x} W_2 &= X_4 (t_w - t_2) \\ \frac{\partial t_w}{\partial \tau} &= X_2(t_1 - t_w) + X_3(t_2 - t_w) \end{aligned}\right\} \qquad \text{(III-19)}$$

A *model of a heat exchanger under unsteady-state conditions, with both fluids under plug-flow conditions* (see Fig. III-2). The following cases may occur:

1. The heat capacity of the separating wall is negligibly small:

– for cocurrent and countercurrent flows:

$$\left.\begin{aligned} \frac{\partial t_1}{\partial \tau} + W_1 \frac{\partial t_1}{\partial x} &= X_1(t_2 - t_1) \\ \frac{\partial t_2}{\partial \tau} \mp W_2 \frac{\partial t_2}{\partial x} &= X_4(t_1 - t_2) \end{aligned}\right\} \qquad \text{(III-20)}$$

– for cross-current flow:

$$\left.\begin{aligned} \frac{\partial t_1}{\partial \tau} + W_1 \left(\frac{\partial t_1}{\partial x} \cos \varphi + \frac{\partial t_1}{\partial y} \sin \varphi \right) &= X_1(t_2 - t_1) \\ \frac{\partial t_2}{\partial \tau} + W_2 \frac{\partial t_2}{\partial x} &= X_4(t_1 - t_2) \end{aligned}\right\} \qquad \text{(III-21)}$$

2. The heat capacity of the separating wall is taken into account:

– for countercurrent and cocurrent flows:

$$\left.\begin{aligned} \frac{\partial t_1}{\partial \tau} \pm W_1 \frac{\partial t_1}{\partial x} &= X_1(t_w - t_1) \\ \frac{\partial t_w}{\partial \tau} &= X_2(t_1 - t_w) + X_3(t_2 - t_w) \\ \frac{\partial t_2}{\partial \tau} \mp W_2 \frac{\partial t}{\partial x} &= X_4(t_w - t_2) \end{aligned}\right\} \qquad \text{(III-22)}$$

— for cross-current flow:

$$\left.\begin{aligned} &\frac{\partial t_1}{\partial \tau}+W_1\left(\frac{\partial t_1}{\partial x}\cos\varphi+\frac{\partial t_1}{\partial y}\sin\varphi\right)=X_1(t_w-t_1)\\ &\frac{\partial t_w}{\partial \tau}=X_2(t_1-t_w)+X_3(t_2-t_w)\\ &\frac{\partial t_2}{\partial \tau}+W_2\frac{\partial t_2}{\partial x}=X_4(t_w-t_2) \end{aligned}\right\} \qquad \text{(III-23)}$$

Rigorous solutions of such equations are either unwieldy or cannot be expressed analytically altogether. The respective transfer functions are transcendental, and their direct analysis is difficult.

Because of this, transients are described by approximate equations having relatively simple analytical expressions which can readily be applied to engineering calculations. Transcendental transfer functions can be approximated to any degree of accuracy with proper fractions, while an approximate estimate of the unit step response function is derived from orthogonal expansions based on the integrals of response curves.

Process optimization. The objective in optimizing a thermal process is to minimize the capital outlays and maintenance cost involved.

The criterion of optimality for heat exchangers is the quantity

$$\Pi = (C_c/T_p)+C_m = \min \qquad \text{(III-24)}$$

where Π is the criterion of optimality, in roubles; C_c represents the capital outlays, in roubles; T_p is the normal pay-off period, in years; and C_m is the maintenance cost.

Design procedure for an optimal heat exchanger. For a given type of heat exchanger, one selects the independent variables whose optimal values are to be found by the design procedure (these may be outlet temperature and tube diameter).

Then the heat transfer surface area, hydraulic resistance, exchanger weight, and pump capacity are expressed in terms of these independent variables. Next, two problems are solved: (1) the relationship between the objective function and the independent variables is established; (2) optimal values for the independent variables are found.

As an example, we shall consider a case where the following conditions are specified: mass flow rate of the hot fluid, G_1; its inlet and outlet temperatures, $t_{1\,in}$, and $t_{1\,out}$, and the inlet temperature, $t_{2\,in}$, of the cold fluid.

The relationship between the mass flow rate of water and the outlet temperature can be deduced from a heat balance. Then the requisite heat transfer surface area is found for each value of water temperature, t_2', t_2'', etc. As will be recalled, the coefficient of heat transfer depends on the velocity of the fluid. Therefore, for each temperature, we should find the requisite heat transfer surface area with different velocities of the fluid in the tubes (w = 0.4 to 2.5 m/s). Then a plot of these data can be constructed (Fig. III-5*a*).

The heat transfer surface area is given by

$$F = nN\pi\, dl$$

where n is the number of passes in the tube bundle, N is the number of tubes in the bundle, l is the length of tubes per pass, d is the tube diameter.

The number N of tubes in the bundle is chosen according to the mass flow rate of the cold fluid:

$$N = \frac{G_2}{w \dfrac{\pi d^2}{4} \gamma_2 3600}$$

Hence,

$$F = n\pi\, dl \frac{G_2}{w \dfrac{\pi d^2}{4} \gamma_2 3600}$$

The mass flow rate of water, G_2, depends on its outlet temperature. With the tube diameter and length specified in advance, we obtain F as a function of the velocity of water for different numbers of tube passes, $n = 2, 4, 6, 8$, etc. For different water outlet temperatures, that is, different mass flow rates of water, we obtain a family of curves (Fig. III-5*b*).

We have already found the relationship between heat transfer surface area and fluid velocity, which satisfies the heat balance. On superimposing

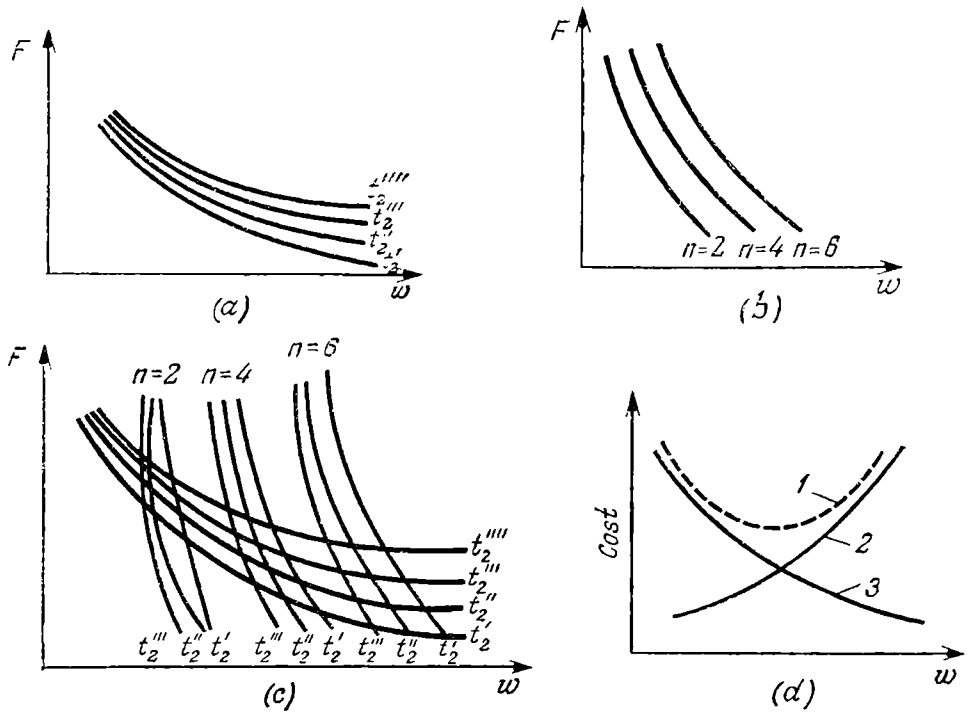


Fig. III-5. To an optimum design of a heat exchanger

(*a*) heat-transfer surface area as a function of amount and flow rate of water; (*b*) heat-transfer surface area as a function of pipe-bundle passes and flow rate of water; (*c*) heat-transfer surface area as a function of amount and flow rate of water and pipe-bundle passes; (*d*) selection of an optimum flow rate of water; 1 — total cost of apparatus; 2 — maintenance costs; 3 — capital outlays

the curves of Figs. III-5*a* and III-5*b*, the intersections define the values of heat transfer surface area satisfying the heat balance, on the one hand, and the requirement for the number of tube passes, on the other, for different fluid velocities (Fig. III-5*c*). Conversely, for different water outlet temperatures and different numbers of tube passes, the intersections define the requisite heat transfer surface area and water velocity.

Now we calculate the water pressure drop in the heat exchanger, the cost (annual depreciation) of the heat exchanger as functions of water velocity, and find annual maintenance costs, and also the minimum cost of the heat exchanger for a given outlet temperature of cooling fluid (Fig. III-5*d*). This calculation is done for several values of $t_{2\,out}$, and the minimum cost is then selected from among the several results.

The result is an optimal design of the heat exchanger: the number of tubes in the bundle, the number of passes, and optimum outlet temperature for water.

Automatic control of heat exchangers. Heat exchangers are indispensable elements of most chemical manufactures, because they are essential to the proper functioning of other units or even whole systems. For example, the functioning of a column depends on the temperature in the reboiler and in the condenser.

Unfortunately, a detailed examination of automatic control systems for heat exchangers is handicapped by the fact that they operate under a wide variety of conditions in chemical engineering. This is why we shall limit ourselves to a few systems most often used in the chemical industry.

As a rule, control of a heat exchanger consists in measuring the output variable (the temperature of one of the fluids) and in varying it by manipulating the flow rate of the other fluid (Fig. III-6*a*).

In cases where the heat-transfer medium, say heating steam, experiences appreciable fluctuations in pressure, use is made of a cascaded control system (Fig. III-6*b*).

Another control system for a heat exchanger is one in which the manipulated variable is the condensate level in the heat exchanger (Fig. III-6*c*). The condensate flooding the tubes affects the heat transfer surface area and, as a consequence, the outlet temperature as desired. This system ensures a maximum steam pressure and temperature in the exchanger; at the same time, the temperature of the outgoing condensate is below the condensation point of steam, which fact improves the coefficient of heat transfer for the heat exchanger.

However, this type of control system cannot maintain a high rate of control action at a reduced thermal load and may therefore be recommended for use only in cases where the system is not subjected to sudden load disturbances.

In systems where no change may be made in the quantity of fluids, use is made of an automatic control system with a bypass (Fig. III-6*d*). With this configuration, the heat transfer surface area must be sufficient to superheat or supercool the controlled fluid so that it can be bypassed.

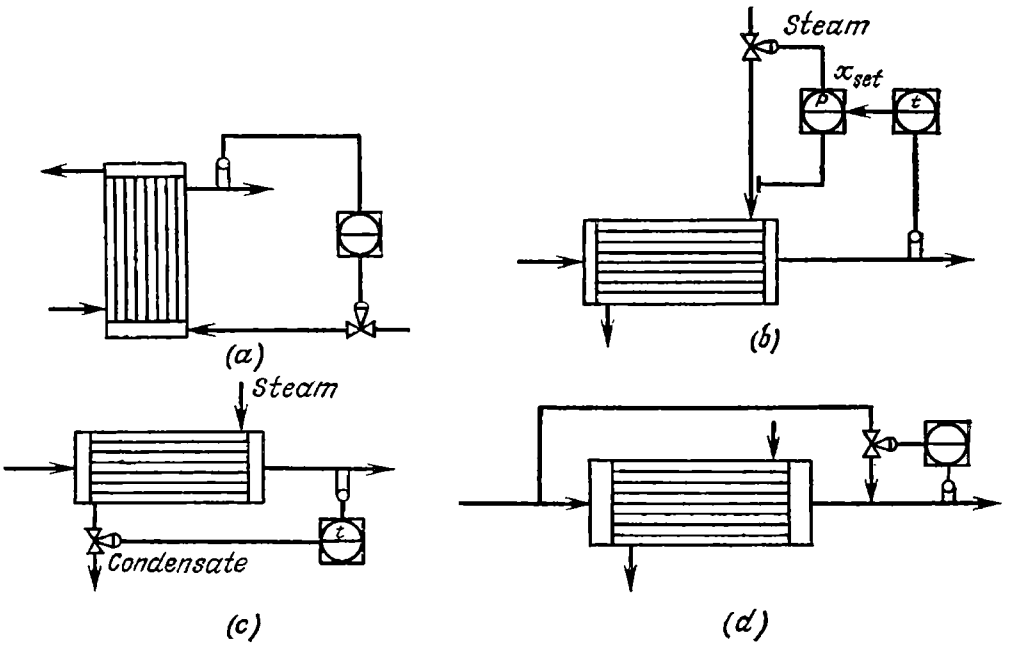


Fig. III-6. Automatic control of heat exchangers
(*a*) single-circuit system; (*b*) cascade system; (*c*) condensate-level control system; (*d*) bypass control system

III-2. MASS TRANSFER PROCESSES

Whether or not a given mathematical model fits a mass transfer process adequately depends above all on our knowledge of the process variables and their interrelations. In a first approximation, assuming a minimum knowledge of these aspects, we may well do with a simplified mathematical model based on general physical considerations or on experimental data. Such a model will throw sufficient light on the interrelations between the various parameters.

On the other hand, a mathematical model overcrowded with detail may entail appreciable computational difficulties, so that even a large-capacity computer will not be able to handle the problem. This is especially true of the optimization and dynamic analysis of complex engineering processes and systems. This is why one must always keep in mind the computational limitations when developing a mathematical model.

As already noted, the development of mathematical models is based on the block-diagram principle. According to this principle, the prototype system is first broken down into "elementary" processes. This approach is particularly well adapted to mass transfer processes.

A mathematical model of a system, developed on the basis of applicable physical relationships, will usually contain the following groups of equations:

– mass and energy balances (continuity equations), with allowance for variations in flow patterns in the prototype system. This group of equations usually describes the distribution of temperature, composition and associ-

ated properties (for example, density, viscosity, heat capacity, and the like) of the flow;

– equations of elementary processes, which define changes in, and interrelations between, the state variables of the flows. This group includes equations of chemical transformations, mass and heat transfer, etc.;

– theoretical, semi-empirical and empirical relations between model parameters, such as the dependence of the coefficient of mass transfer on the velocities of phase flows, the dependence of solution density on composition, etc.

A mathematical model will also include various constraints or restrictions on the applicability of empirical relations, on the range of changes in some of the variables, etc.

(A) ABSORPTION IN PACKED COLUMNS

Mathematical models for absorption in packed columns may be divided into two broad groups:[2] (1) models without longitudinal mixing and (2) models with longitudinal mixing. The first group (Table III-1) encompasses columns operating under conditions of plug flow for all interacting phases.

In the general case, transfer under unsteady-state conditions is described by a system of simultaneous nonlinear partial differential equations of the form

$$\left.\begin{aligned} L\frac{\partial x}{\partial z}+K_V(L,G)\,\Delta c &= h_L(L,G)\frac{\partial x}{\partial \tau} \\ G\frac{\partial y}{\partial z}+K_V(L,G)\,\Delta c &= -h_G(L,G)\frac{\partial y}{\partial \tau} \end{aligned}\right\} \qquad \text{(III-25)}$$

where G and L are the mass flow rates for the gaseous and liquid phases through the full section of the column, in kg m^2 h^{-1}; x and y are the component concentrations in the liquid and gaseous phases, in kg kg or %; Δc is the process driving force, kg/kg; K_V is the volumetric coefficient of mass transfer, kg m^{-3} h^{-1} (kg/kg)$^{-1}$; h_L and h_G are the liquid and gas holdup, kg/m^3; τ is the time, h; and z is the depth of the packing, m.

These equations are nonlinear because their coefficients depend on the magnitude of disturbances. An analytical solution of such a system would run into unsurmountable difficulties and can only be obtained on making some simplifying assumptions.

One such assumption is to deem the coefficients in the equation of the mathematical model constant if the behaviour of the process is examined under conditions of small perturbations from the steady state. Another simplification is to average the driving force of the process over the height of the column. Then the original system of simultaneous partial differential equations will reduce to a system of ordinary differential equations.

In a first approximation, changes in the phase concentrations with the height of the column can be approximated by a linear relation, and the average concentrations may be expressed as the arithmetic means of their

Mathematical Models for Absorption Processes

Model No.	Classification	Equations	Transfer functions	Notation
		Longitudinal mixing ignored		
1	Lumped-parameter (arithmetic-mean driving force)	$G(y_{in}-y_{out})+\Delta G(y^0_{in}-y^0_{out})-L(x_{out}-x_{in})=\frac{h_L}{2}x^0_{out}\frac{dx_{out}}{d\tau}+\frac{h_L}{2}x^0_{in}\frac{dx_{in}}{d\tau}+\frac{h_G}{2}y^0_{out}\frac{dy_{out}}{d\tau}+\frac{h_G}{2}y^0_{in}\frac{dy_{in}}{d\tau}$ $G(y_{in}-y_{out})+\Delta G(y^0_{in}-y^0_{out})=\frac{h_G}{2}y^0_{in}\frac{dy_{in}}{d\tau}-\frac{h_G}{2}y^0_{out}\frac{dy_{out}}{d\tau}=\frac{K_v}{2}\times(y_{in}-mx_{out}+y_{out}-mx_{in})$	$W_G(p)=K\frac{T_1p+1}{T_2p+1}$ at $h_G=0$, $h=h\cdot z$	$T_1=\frac{h_L}{K_vZm+2L}$ $T_2=\frac{h_LK_v+2G_0h_L}{R}$ $K=\frac{K_vmz+2L}{R}$ $R=K_vZ(mG_0-L)+2LG_0$
2	Theoretical plate	$G(y_{n-1}-y_n)+L(x_{n+1}-x_n)=h_L\frac{dx_n}{d\tau}+h_G\frac{dy_n}{d\tau}$	$W_y(p)=-\frac{T_G\sqrt{b^2-4T_LT_G}}{h(D_2^N-D_1^N)-T_LT_G(D_2^{N-1}-D_1^{N-1})}$	$T_L=\frac{L}{m}$, $T_G=G$ $D_{1,2}=\frac{1}{2}\times(b\pm\sqrt{b^2-4T_LT_G})$
3	Multi-stage representation (staged linearization of driving force)	$G(y_{n-1}-y_n)+\Delta G(y^0_{n-1}-y^0_n)-L(x_n-x_{n+1})=\frac{h_L}{2N}x^0_n\frac{dx_n}{d\tau}+\frac{h_L}{2N}x^0_{n+1}\frac{dx_{n+1}}{d\tau}+\frac{h_G}{2N}y^0_{n-1}\frac{dy_{n-1}}{d\tau}$ $G(y_{n-1}-y_n)+\Delta G(y^0_{n-1}-y^0_n)-\frac{h_G}{2N}y^0_{n-1}\frac{dy_{n-1}}{d\tau}-\frac{h_G}{2N}y^0_n\frac{dy_n}{d\tau}=\frac{K_vZ}{2N}(y_{n-1}-mx_n+y_n-mx_{n+1})$	—	—

Table III-1 (continued)

Model No.	Classification	Equations	Transfer functions	Notation
4	Distributed-parameter (logarithmic-mean driving force)	$L\frac{\partial x}{\partial z}+K_v(y-y^*)=h_L\frac{\partial x}{\partial \tau}$ $G\frac{\partial y}{\partial z}+K_v(y-y^*)=-h_G\frac{\partial y}{\partial \tau}$	$W_v(p)=\frac{e^{s_1 z}e^{s_2 z}(\beta_1-\beta_2)}{e^{s_1 z}\beta_1-e^{s_2 z}}$	$\beta_1=\frac{Gs_1}{K_v m}+\frac{1}{m}+\frac{h_G P}{K_v m}$ $\beta_2=\frac{Gs_2}{K_v m}+\frac{1}{m}+\frac{h_G P}{K_v m}$ $x_{1,2}$ — roots of characteristic equation
		With allowance for longitudinal mixing		
5	Fully asymmetrical model	$G\frac{\partial y}{\partial z}+K_v(y-y^*)=-h_G\frac{dy}{d\tau}$ $L\bar{x}+K_v(y-y^*)=h_L\frac{d\bar{x}}{d\tau}$ where $\bar{x}=\frac{1}{Z}\int_0^Z x\,dz$	$W_v(p)=K_{\exp}\left(\frac{K'}{Tp+1}\right)$ at $h_G=0$	$K=\exp\left(\frac{K_v Z}{G}\right)$ $K'=\frac{mK_v^2 Z_2}{GK_v m\bar{Z}-LG}$ $T=\frac{h_L Z}{K_v m\bar{Z}-L}$
6	Asymmetrical model	$L(x_{n,k+1}-x_{n,k})+\frac{K_v Z}{aN}(y_n-mx_{n,k})=\bar{h}_L\frac{dx_{n,k}}{d\tau}$ $G(y_{n-1}-y_n)-\frac{K_v Z}{N}(ay_n-m\sum^a x_{n,k})=\bar{h}_G\frac{dy_n}{d\tau}$	--	—

Table III-1 (continued)

Model No.	Classification	Equations	Transfer functions	Notation
7	Symmetrical model	$L(x_{n+1}-x_n)+\frac{K_vZ}{N}(x_n^*-x_n)=h_L\frac{dx_n}{d\tau}$, $G(y_{n-1}-y_n)-\frac{K_vZ}{N}(x_n^*-x_n)=h_G\frac{dy_n}{d\tau}$	$W_y(p)$ $=\frac{T_L^N\sqrt{(T_LT_G-d+1)^2-4T_LT_G}}{(T_LT_G-d)(D_2^N-D_1^N)-T_LT_G\times(D_2^{N-1}-D_1^{N-1})}$	$T_L=\left(\frac{Zh_L}{L}p+\frac{K_vZ}{L}+1\right)$, $d=\left(\frac{K_vZ}{LGm}\right)^2$, $T_G=\left(\frac{Zh_G}{G}p+\frac{K_vZ}{Gm}+1\right)$, $D_{1,2}=\frac{1}{2}[(T_LT_G-d+1)\pm\sqrt{(T_LT_G-d+1)-4T_LT_G}]$
8	Fully symmetrical	Plug flow, Well stirred: See model 4 $G(y_{in}-y_{out})=K_vZ(y_{out}-y_{out}^*)=h_G\frac{dy_{out}}{d\tau}$, $L(x_{in}-x_{out})+K_vZ(y_{out}-y_{out}^*)=h_L\frac{dx_{out}}{d\tau}$	See model 4 $W_y(p)=\frac{Gm(Zh_Lp+T_L)}{Zh_GT_Gp+[T_LT_G-(K_vZ)^2]}$	— $T_G=K_vZ+mG$, $T_L=K_vZ+L$

initial and final values (see Table III-1, Model 1). In the case of an unsteady-state behaviour, however, when the driving force may be doubled or halved with height, this simplification may result in major departures from an exact solution. If so, use must be made of the logarithmic mean of the driving force (Model 4).

Another technique for analysis of distributed systems, usually employed where models are computer-solved partial differential equations, is based on simulating a continuous process by a batch one, with lumped parameters in each stage. Depending on the assumptions made as regards the mechanism of mass transfer in each stage, and also according to the presentation of the driving force, several mathematical models are feasible (Models 2 and 3).

The simplest one is a model which ignores the kinetics of absorption. The packed absorber is treated as a plate column with plates having an efficiency of unity (Model 2). The number of plates is chosen to be equal to the number of stages, each equivalent to one theoretical plate.

From dynamic analysis of packed columns on the basis of this model it has been found that with a small number of stages (theoretical plates), the delay region is shown inadequately on the time response curve of the process. Besides, the steady-state behaviour can be calculated only with some approximation, because the number of stages (theoretical plates) cannot be a fraction.

The material balance is satisfied by a model which allows for the kinetics of the process. The packed bed is arbitrarily divided into a number of stages which exceeds the number of stages of complete separation (theoretical plates). From an unsteady-state analysis of the process on the basis of this model (Model 3) in which the driving force of a stage is an arithmetic mean, or the values existing at the top or bottom, it has been found that this model fits the unsteady-state properties of the actual process inadequately.

In all of the above models, it is assumed that the plug-flow condition applies to all interacting phases. They only differ in the approximation of the driving force which tends in the limit to a logarithmic mean distribution. For example, if we choose the multi-stage model of the process, the adequacy of the mathematical model will improve with an increase in the number of stages, n, that is, as the model approaches the plug-flow regime. In turn, the plug flow is an idealization for actual reactors, and the closeness of fit to this ideal depends on the hydrodynamic conditions under which the packed absorber operates. In actual absorbers, the fluid elements differ in the residence time distribution because of variations in the velocity profiles, molecular diffusion and turbulence.

Longitudinal mixing is one of the major factors affecting the static (steady-state) and dynamic (unsteady-state) behaviour of packed columns, and the extent of this effect depends on the flow pattern prevailing in the reactor. In developing a mathematical model for a packed column as a distributed-parameter entity with allowance for longitudinal mixing, two approaches

are possible. One is to use a dispersion model described by partial differential equations. The other is to use a cascade model which is an approximation of a continuous process with a multi-stage one having lumped parameters in each stage.

Before we attempt to examine these models, we shall introduce the concept of longitudinal symmetry in a reactor. The flows are called symmetrical if the respective phases have the same degree of longitudinal mixing. The extent of longitudinal mixing may be evaluated either in terms of the number of stirred single tanks, n, or in terms of the longitudinal dispersion number, D_L. Then the mathematical models for absorption in packed columns may be classed as follows:

symmetrical models for which $n_L = n_G = N$
asymmetrical models for which $n_L \neq n_G$; $n_L = N_L$; $n_G = N_G$
fully symmetrical models for which $n_L = n_G = \infty$ or unity
fully asymmetrical models for which $n_L \neq n_G$; $n_L = 1$; $n_L = \infty$ or $n_L = \infty$; $n_G = 1$

A mathematical model which allows for the flow patterns of the interacting phases fits more adequately the process occurring in a two-phase system.

With a cascade model, a packed absorber is treated as a system of stirred tank units between which mass transport takes place. The number of units for each phase depends on the extent of longitudinal mixing of the respective phase. Two limiting cases may occur: perfect mixing in the liquid phase and a plug flow in the gas phase, or vice versa. As regards packed absorbers, the former case is of special interest.

A cascade model is described by a system of simultaneous difference-differential equations which can be solved with relative ease on a digital computer. Since the model is an assemblage of blocks, it can readily be analysed in terms of Boolean algebra and simulated on an analog computer. Besides, the transfer functions for symmetrical and fully asymmetrical models can readily be obtained analytically for further use in the analysis and synthesis of automatic control systems for packed columns. Owing to these advantages, the cascade model takes precedence over the dispersion model in tackling control problems. The derivation of the basic equations of the cascade model in the form of transfer functions which describe the dynamics of absorption in packed columns follows.[3]

Symmetrical cascade model. The flow diagram of absorption is based on a material balance under unsteady-state conditions.

Fast dissolving gases. The flow pattern for the ith stage is shown in Fig. III-7. For fast dissolving gases it is assumed that the resistance to mass transport is

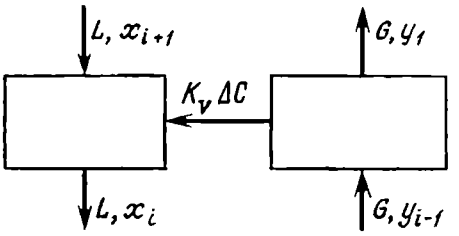


Fig. III-7. Block-diagram presentation of material streams for an ith stage of a cascade model

offered by the gas phase, and the driving force of the process is written in terms of this phase as follows

$$\Delta y = y_i - y_{eq} = y_i - mx_i$$

The behaviour of the ith stage is described by the following equations:
– a material balance on the liquid phase

$$-Lx_i + Lx_{i+1} + K_V H(y_i - y_{eq}) = h_L H \frac{dx_i}{d\tau} \qquad \text{(III-26)}$$

– a material balance on the gas phase

$$Gy_{i-1} - Gy_i - K_V H(y_i - y_{eq}) = h_G H \frac{dy_i}{d\tau} \qquad \text{(III-27)}$$

Henry's law

$$y_{eq} = mx_i \qquad \text{(III-28)}$$

where y_{eq} is the equilibrium concentration of the gas phase and H is the height of the stage.

Solving Eqs. (III-26) and (III-28) simultaneously and taking their Laplace transforms, we obtain

$$-L\bar{x}_i + L\bar{x}_{i+1} + K_V H(\bar{y}_i - m\bar{x}_i) = h_L H \bar{x}_i p \qquad \text{(III-29)}$$

The transfer function of the $x_i - x_{i+1}$ circuit is

$$W_1(p) = \frac{K_1}{T_1 p + 1} \qquad \text{(III-30)}$$

where

$$K_1 = \frac{L}{K_V Hm + L}$$

$$T_1 = \frac{h_L H}{K_V Hm + L}$$

The transfer function for the $x_i - y_i$ circuit is

$$W_2(p) = \frac{K_2}{T_2 p + 1} \qquad \text{(III-31)}$$

where

$$K_2 = \frac{K_V H}{K_V Hm + L}$$

$$T_2 = T_1$$

Solving Eqs. (III-27) and (III-28) simultaneously and taking their Laplace transforms, we obtain

$$G\bar{y}_{i-1} - G\bar{y}_i - K_V H(\bar{y}_i - m\bar{x}_i) = h_G H \bar{y}_i p \qquad \text{(III-32)}$$

The transfer function of the $y_i - x_i$ circuit is

$$W_3(p) = \frac{K_3}{T_3 p + 1} \qquad \text{(III-33)}$$

where

$$K_3 = \frac{K_V Hm}{K_V H + G}$$

$$T_3 = \frac{h_G H}{K_V H + G}$$

The transfer function for the $y_i - y_{i-1}$ circuit is

$$W_4(p) = \frac{K_4}{T_4 p + 1} \qquad \text{(III-34)}$$

where

$$K_4 = \frac{G}{K_V H + G}$$

$$T_4 = T_3$$

The above transfer functions provide a basis on which to draw a block-diagram for the ith stage. Obviously, the column will consist of n stages connected in series. A block-diagram for the absorption process is shown in Fig. III-8.

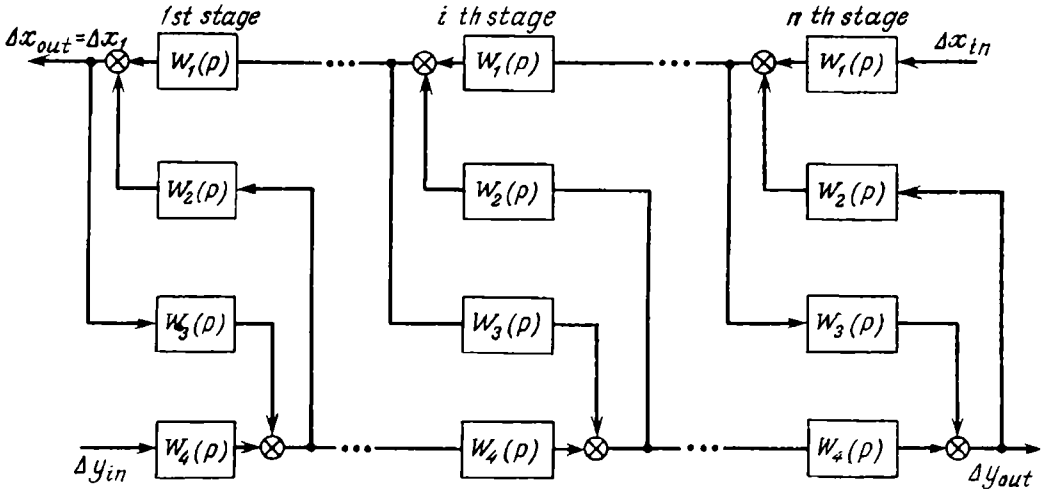


Fig. III-8. Block-diagram of an absorption model

Figure III-9 is a set-up diagram for simulation of the absorption process on an analog computer. To minimize the number of integrators it may be assumed that in Eq. (III-27) the gas hold-up is zero very nearly (actually, it is 2 to 3% of the dynamic hold-up) because of the low density of the gas phase.

The transfer functions $W_3(p)$ and $W_4(p)$ derived at $h_G = 0$ are similar to those of pure-gain elements

$$W_3(p) = K_3 \qquad \text{(III-35)}$$

$$W_4(p) = K_4 \qquad \text{(III-36)}$$

where K_3 and K_4 are similar to the respective quantities derived earlier.

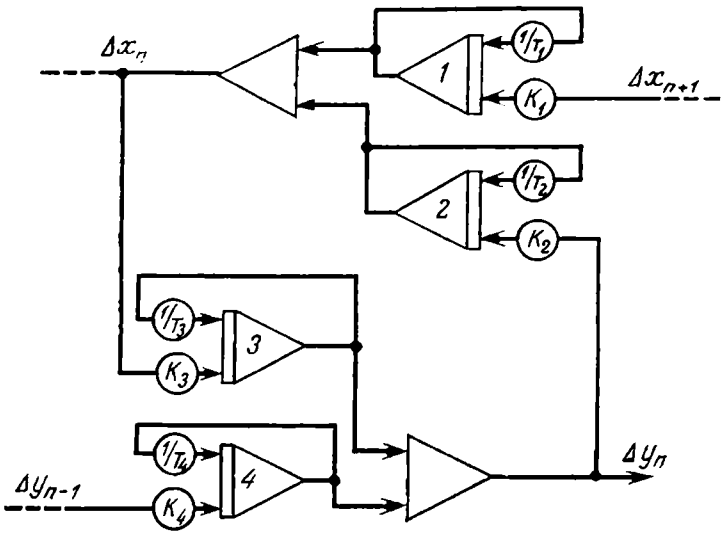


Fig. III-9. Analog computer implementation of a cascade model

Slowly dissolving gases. In contrast to fast dissolving gases, the driving force is now written as follows

$$\Delta x = x_{eq} - x_i = \frac{y_i}{m} - x_i$$

The behaviour of the ith stage is described by the following equations:

– for the liquid phase:

$$-Lx_i + Lx_{i+1} + K_y H(x_{eq} - x_i) = h_2 H \frac{dx_i}{d\tau} \qquad \text{(III-37)}$$

– for the gas phase:

$$Gy_{i-1} - Gy_i - K_y H(x_{eq} - x_i) = h_G H \frac{dy_i}{d\tau} \qquad \text{(III-38)}$$

– the equilibrium relation:

$$x_{eq} = y_i/m \qquad \text{(III-39)}$$

By similar manipulations and transformations, we obtain for slowly dissolving gases the following transfer functions:

$$W_1(p) = \frac{\bar{x}_i}{\bar{x}_{i+1}} = \frac{K_1}{T_1 p + 1} \qquad \text{(III-40)}$$

where

$$K_1 = \frac{L}{K_y H + L} \qquad T_1 = \frac{h_L H}{K_y H m + L}$$

$$W_2(p) = \frac{\bar{x}_i}{y_i} = \frac{K_2}{T_2 p + 1} \qquad \text{(III-41)}$$

where

$$K_2 = \frac{K_V H}{m(K_V H + L)} \qquad T_2 = \frac{h_L H}{K_V H + L}$$

$$W_3(p) = \frac{\bar{y}_i}{\bar{x}_i} = \frac{K_3}{T_3 p + 1} \tag{III-42}$$

where

$$K_3 = \frac{K_V H m}{Gm + K_V H} \qquad T_3 = \frac{h_G H m}{Gm + K_V H}$$

$$W_4(p) = \frac{\bar{y}_i}{\bar{y}_{i-1}} = \frac{K_4}{T_4 p + 1} \tag{III-43}$$

where

$$K_4 = \frac{Gm}{Gm + K_V H} \qquad T_4 = T_3$$

The block-diagram and analog computer implementation for slowly dissolving gases are similar to those for fast dissolving gases.

Analysis of the cascade model under steady-state conditions. The volumetric coefficient of mass transfer varies, depending on the degree of longitudinal mixing. Its calculation from the logarithmic-mean driving force holds only under plug-flow conditions, that is, with the number of stages tending to infinity. The volumetric coefficient of mass transfer is given by

$$G(y_{in} - y_f) = K_V \frac{(y_{in} - y_{eq}) - (Y_f - y_{eq})}{2.3 \log_{10} \dfrac{y_{in} - y_{eq}}{y_f - y_{eq}}} l \tag{III-44}$$

where y_{in} and y_f are the initial and final concentrations, y_{eq} is the equilibrium concentration, and l is the length of packing.

For the other limiting case, that is, well-stirred or perfect-mixing conditions, $n = 1$. The coefficient of mass transfer can readily be found from the following relation

$$K_V = \frac{LG(1-\alpha)}{\alpha LH - HGm(1-\alpha)} \tag{III-45}$$

where α is the slope of the static (steady-state) characteristic curve, $y_f = f(y_{in})$, and m is the Henry law constant.

If $1 < n < \infty$, the mass-transfer coefficient, K_V, can be found from the steady-state characteristic of the cascade model by substituting $p = 0$ in its transfer function. Then the steady-state characteristic takes the form of a polynomial of the nth power about the mass-transfer coefficient:

$$A(n)K_V^n + B(n)K_V^{n-1} + \ldots + E(n)K_V + F(n) = 0 \tag{III-46}$$

An algebraic equation of the nth order has n roots, of which n_1 are real roots, and n_2 are imaginary roots. The imaginary roots have no physical significance and are therefore dropped. The real roots occupy a range of

values

$$K_{V\,\min} < K_V < K_{V\,\max}$$

where $K_{V\,\min}$ represents plug-flow conditions, and $K_{V\,\max}$ perfect-mixing conditions.

For each number of stages there is a certain definite coefficient of mass transfer. The relationship between the volumetric coefficient of mass transfer and the number of stages for a specified degree of separation can be obtained by solving Eq. (III-46) on a digital computer.

From a multitude of experiments, it has been found that on approaching the point of inversion, the velocity profiles of the gas and liquid phases across the section of the column are equalized and the column comes to operate under conditions of plug flow.

(B) CONTINUOUS RECTIFICATION IN PLATE COLUMNS

A rectifying plant is in effect a combination of several units: a column (or tower), a still or reboiler, and a condenser. In operation, the three units are traversed by common streams of a liquid and its vapour. Failure to fit adequately a mathematical model to any of the three units may well mean a failure for the overall model of the process. Therefore, the various mathematical models of rectifying units incorporate groups of equations describing the respective stages of the process. The models may differ in the completeness of coverage according to particular applications.

The equations most characteristic of the various types of models for plate rectifying units are presented in Table III-2.[4] The table covers only six markedly differing models. Most of the rectifying units in current use may be identified with one of the types included. In many cases, the difference is only in the expression of thermodynamic relations and in the algorithms for solving the model equations.

To make the classification more meaningful, the functional groups of equations describing the same steps of the process in different models are collected together.

The basic group of equations essential to developing any model are those describing the interphase transfer of the mixture components. Practically, these are equations from which one can determine the composition of the vapour phase leaving a separation stage from the known composition of the liquid present and the composition of the entering vapour. This is an extremely complicated relationship; yet, it is crucial in calculations.

As follows from Table III-2, the well-stirred and cascade models are chosen for the liquid phase, while the gas phase is considered under conditions of plug flow and complete mixing. Complete mixing has been chosen for the vapour phase because it fits the assumption that it condenses on the plate, which is plausible within the framework of the theoretical plate concept.

Mathematical models for rectifying columns based on the theoretical plate concept are widely used in design work because they make unnecessary knowledge of the flow pattern on the plates. In effect, such models (Models

3,5 and 6 in Table III-2) are an attempt to describe a vessel with complete condensation of the vapour phase at the separation stages, rather than a rectifying column.

To some extent, this reflects the properties of rectification, because the interaction of the vapour and liquid phases is accompanied by condensation. Yet, this approach ignores the interphase mass transfer which cannot but affect the behaviour of the rectifying column.

In contrast, in another group of models (Models 1, 2 and 4 in Table III-2), condensation or vaporization is not regarded as the main mechanisms of separation, and the mass transfer between phases is presented as an outcome of only diffusion. Obviously, this approach cannot be adopted as the sole method for modeling the separation process. Yet, it leaves room for the effect of the flow pattern on the plates and, what is perhaps most important, establishes a univalued relationship between actual plates and their representation in a model.

In one form or another, mathematical models include a group of equations describing the equilibrium relationships between the liquid and vapour phases. The adequacy of these relationships in representing the actual equilibrium of a practical mixture has a direct bearing on the accuracy of modeling and, as a consequence, on predictions of the behaviour of the real column.

For the most part, the equilibrium of multicomponent mixtures is described by equilibrium relations expressed in terms of the equilibrium constants or the relative volatility of the components. Then, the vapour composition which is in equilibrium with a known liquid composition is given by

$$y^*_{i,k} = k_k(t_i)x_{i,k} \qquad \text{(III-47)}$$

where $k_k(t_i)$ is the equilibrium constant which is a function of the temperature and pressure at the ith separation stage.

The temperature at the ith stage is found by solving the equation

$$\sum y^*_{i,k} = \sum k_k(t_i)x_{i,k} = 1 \qquad \text{(III-48)}$$

Generally, the form of the function $k_k(t_i)$ that holds for a component in a given mixture will not hold for it in just any mixture. This is why, in analysing the separation of a particular mixture, one is forced to use equilibrium data obtained specifically for that mixture. Even then, the danger of error remains, because a function of the form given by (III-47) cannot describe a state of equilibrium for a mixture with a widely varying composition, since no account is taken of the interaction between the components in real mixtures. It is only in the case of binary mixtures that a relation of the form (III-48) can be readily specified — the properties of a binary mixture at boiling point are uniquely characterized by the concentration of only one component. In such cases, equilibrium data can be presented as a function of the mixture composition, if appropriate experimental data are available.

A clear-cut delineation of all mathematical models for rectification into two groups can be made on the basis of heat balances around separation

Column model	$i \mid \frac{L_{i+1} + x_{k,i+1}\bar{x}_i + U_i V_i + y_{k,i}}{L_i + x_{k,i}\bar{x}_{i-1} + U_{i-1}V_{i-1} + y_{k,i-1}} \mid$		
	flow patterns on plate	mass	
		kinetic relations	equilibrium relation
1 Binary mixture	Complete mixing for liquid; plug flow for vapour	$K_{0y}^{(i)} = \frac{1}{\frac{1}{K_{yi}} + m_i \frac{1}{K_{xi}}}$ $K_{x,i} = K_{xi}(L_i, V, x_i)$ $K_{y,i} = K_{yi}(L_i, V, x_i)$ $m_i = \frac{dy_i^*}{dx_i}$	$y_i^* = y_i^*(x_i)$ $y_i^* = \frac{(a+bx_i)x_i}{1+(c+dx_i)x_i}$
2 Same	Well-stirred stages in cascade for liquid; plug flow for vapour	$N_{0y}^{(i)} = \frac{L_i N_x^{(i)} N_y^{(i)}}{L_i N_x^{(i)} + m_i V_i N_y^{(i)}}$ $N_y^{(i)} = \alpha_y^{(i)} + K_y^{(i)} V_i + \gamma_y^{(i)} L_i$ $N_x^{(i)} = (\alpha_x^{(i)} + K_x^{(i)} V_i + \gamma_x^{(i)} L_i) \times (1 + \varepsilon_x^{(i)} V_i) \frac{1}{L_i}$	
3 Multicomponent mixture	Complete mixing for liquid; same for vapour	Phase equilibrium (theoretical stage)	$y_{k,i}^* = k_{k,i} x_{k,i}$ $k_{k,i} = k_k(p_i, T_i)$
4 Same	Complete mixing for liquid; plug flow for vapour	$N_{kl}^{(i)} = \frac{L N_{x,k,l}^{(i)} N_{y,k,l}^{(i)}}{L N_{x,k,l}^{(i)} + m_i V N_{y,k,l}^{(i)}}$ $m_i = \frac{\partial y_i^*}{\partial x_i}$ for $N_{x,k,l}^{(i)}, N_{y,k,l}^{(i)}$ see Model 2	$y_{k,i}^* = k_{k,i} x_{k,i}$ $k_{k,i} = \sum_{b=1}^{m} a_{k,l} T_i^l$

Plate Rectifying Columns

Stage of separation		
transfer	balances	
composition of vapour leaving given stage	overall balance on phase streams	balances on mixture components
$y_i = y_{i-1}e^{-\frac{K_{0y}^{(i)}}{V}} + y_i^*\left(1-e^{-\frac{K_{0y}^{(i)}}{V}}\right)$	$L_i = U_{i-1}+V+W$ $i = 1, \ldots, f$	$L_ix_i = Vy_{i-1}+U_{i-1}x_{i-1}+Wx_0$ $i = 1, \ldots, f$
	$L_i = U_{i-1}+V-D$ $L_i = f+1, \ldots, N+1$	$L_ix_i = Vy_{i-1}+U_{i-1}x_{i-1}-Dy_{N+1}$ $i = f+1, \ldots, N+1$
$y_i = \frac{V_{i-1}}{V_i}\left[y_{i-1}+(y_i^*-y_{i-1})\eta_{T_i}\right] + \frac{V_i-V_{i-1}}{V_i}\,\Omega_i$	$L_i = V_{i-1}+U_{i-1}+W$ $i = 1, \ldots, f$	$L_ix_i = V_{i-1}y_{i-1}+U_{i-1}\bar{x}_{i-1}+Wx_0$ $i = 1, \ldots, f$
$\Omega_i = \left[\left(\frac{2}{m_i}-\frac{a-1}{a}\frac{V_{i-1}}{L_i}\eta_0^{(i)}\right)\times(y^*-y_{i-1})-x_i+\omega_i\right]\frac{\eta_{T_i}}{\eta_0^{(i)}} - \left[\frac{2(y_i^*-y_{i-1})}{m_i}-x_i\right]$	$L_i = V_{i-1}+U_{i-1}+W-F$ $i = f+1, \ldots, N+1$	$L_ix_i = V_{i-1}y_{i-1}+U_{i-1}\bar{x}_{i-1}+Wx_0-Fx_F$ $i = f+1, \ldots, N+1$
$\eta_{iT_i} = \frac{\left(1+\frac{V_{i-1}m_i}{L_ia}\eta_0^{(i)}\right)^a-1}{m_iV_{i-1}}L_i$		
$\eta_{i0}^{(i)} = 1-e^{-N_{0y}^{(x)}}$ $y_{k,i} = y_{k,i}^*$	L and V specified	$Lx_{k,i} = Vy_{k,i-1}+Wx_{k,0}$ $i = 1, \ldots, f$ $Lx_{k,1} = Vy_{k,i-1}-Dx_{k,N+1}$ $i = f+1, \ldots, N+1$ $k = 1, \ldots, n$
$y_{k,i} \cong y_{k,i-1}e^{-N_{k,i}}+y_{k,i}^*\times(1-e^{-N_{k,i}})\delta_{k,i}$ $N_{k,i} = \sum_{\substack{l=1\\l\neq k}}^{n}{}' N_{k,l}^{(i)}y_{l,i}^* + \frac{\sum_{l=1}^{n}{}' N_{k,l}^{(i)}y_{l,i-1}}{\sum_{l=1}^{n}{}' y_{l,i-1}}\,y_{k,i}^*$ $\delta_{k,i} = \frac{\sum_{l=1}^{n}{}' N_{k,l}^{(i)}y_{l,i-1}}{N_{k,i}\sum_{l=1}^{n}{}' y_{l,i-1}}$	L and V specified	$Lx_{k,i} = Vy_{k,i-1}+Wx_{k,0}$ $i = 1, \ldots, f$ $Lx_{k,i} = Vy_{k,i-1}+Wx_{k,0}-Fx_{k,F}$ $i = f+1, \ldots, N+1$ $k = 1, \ldots, n$

Table III-2 (continued)

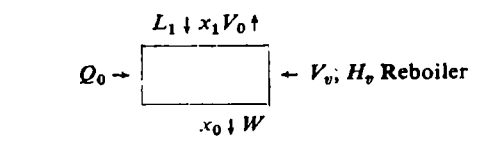
Column model	i $\frac{L_{i+1} \downarrow x_{k,i+1}\bar{x}_i \uparrow U_i V_i \uparrow y_{k,i}}{L_i \downarrow x_{k,i}\bar{x}_{i-1} \uparrow U_{i-1}V_{i-1} \uparrow y_{k,i-1}}$		
	flow patterns on plate	mass	
		kinetic relations	equilibrium relation
5 Multi-component mixture	Complete mixing for liquid; same for vapour	Phase equilibrium (theoretical stage)	See Model 3
6 Same	Complete mixing for liquid; same for vapour	Same	See Model 3

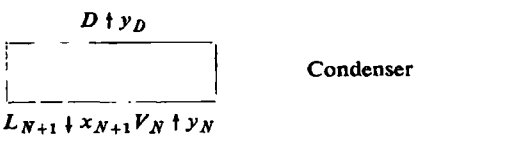
Table III-2 (continued)

Column model	Column		
	thermal balance	liquid entrainment	phase enthalpy and temperature
1	—	$U_i = U(x_i, y_i, V_i, L_i)\ U_N = 0$	—
2	$L_i h_i - V_{i-1}H_{i-1} - U_{i-1}h_{i-1} + Q_0 + V_v H_v - W h_0 = 0$ $i = 1, \ldots, f$ $L_i h_i - V_{i-1}H_{i-1} - U_{i-1}h_{i-1} + Q_0 + V_v H_v - W h_0 + F\bar{H}_F = 0$ $i = f+1, \ldots, N+1$	$U_i = A_i(V_i)^{4.2}$ $A_i = \frac{0.276 \times 10^{-8}}{\sigma_i (S_T)^{3.2}}$	$h_i = h_l x_i + h_h(1-x_i)$ $H_i = H_l y_i + H_h(1-y_i)$ $T_{yi} = \sum_{l=0}^{m} a_l y_i^l$ $T_{xi} = \sum_{l=0}^{m} a_l (y_i^*)^l$

Stage of separation

transfer	balances	
composition of vapour leaving given stage	overall balance on phase streams	balances on mixture components
$v_{k,i} = S_{k,i} l_{k,i}$; $S_{k,i} = k_{k,i} \frac{V_i}{L_i}$ $i = 1, \ldots, f$ $v_{k,i} = \frac{1}{A_{k,i}} l_{k,i}$; $A_{k,i} = \frac{1}{k_{k,i}} \frac{L_i}{V_i}$ $i = f+1, \ldots, N+1$	$L_i = V_{i-1} + W$ $i = 1, \ldots, f$ $L_i = V_{i-1} + W - F$ $i = f+1, \ldots, N+1$	$l_{k,i} = v_{k,i-1} + l_{k,0}$ $i = 1, \ldots, f$ $l_{k,i} = v_{k,i-1} + l_{k,0} - l_{k,F}$ $i = f+1, \ldots, N+1$ $k = 1, \ldots, n$
	$L_i = \sum_{k=1}^{n} l_{k,i}$	
$y_{k,i} = \frac{v_{k,i}}{V_i}$; $x_{k,i} = \frac{l_{k,i}}{L_i}$	$V_i = \sum_{k=1}^{n} v_{k,i}$	
See Model 3	$L_i = V_{i-1} + W$ $i = 1, \ldots, f$ $L_i = V_{i-1} + W - F$ $i = f+1, \ldots, N+1$	$L_i x_{k,i} = V_{i-1} y_{k,i-1} + W x_{k,0}$ $i = 1, \ldots, f$ $L_i x_{k,i} = V_{i-1} y_{k,i-1} - D y_{k,N+1}$ $i = f+1, \ldots, N+1$ $k = 1, \ldots, n$



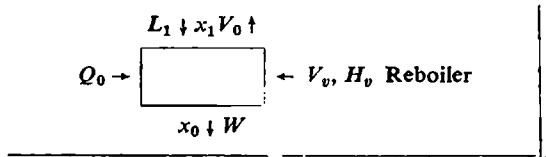


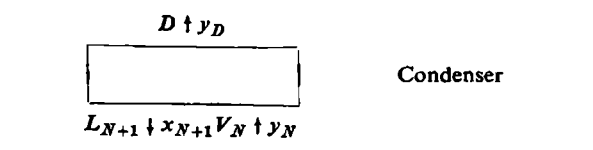
type	vapour composition	type	distillate and reflux composition
Partial	$y_0 = y_0^*(x_0)$	Total	$y_D = x_{N+1} = y_N$
1. Partial	1. $y_0 = y_0^*(x_0)$	1. Total	1. $y_D = x_{N+1} = y_N$
2. Total	2. $y_0 = x_0 = x_1$	2. Partial	2. $y_D = y_N(1-E_D) + y_{N+1}^*(x_{N+1}) E_D$
3. Live steam	3. $y_0 = y_0^*(x_0) \frac{1}{1 + \frac{\psi}{1-\psi} \frac{H_0}{H_v}}$		$x_{N+1} = \frac{1}{L_{N+1}} (V_N y_N - D y_D)$

Table III-2 (continued)

Column model	Column		
	thermal balance	liquid entrainment	phase enthalpy and temperature
3	—	—	$\sum_{k=1}^{h} k_{k,i}(T_i)x_{k,i} = 1$
4	—	—	See Model 3
5	$L_i h_i + V_i H_i - L_{i+1}h_{i+1} - V_{i-1}H_{i-1} = 0$ $i = 1, \ldots, N \quad i \neq f$ $L_i h_i + V_i H_i - L_{i+1}h_{i+1} - V_{i-1}H_{i-1} - F\bar{H}_F = 0$ $i = f$	—	$L_i h_i = \sum_{k=1}^{h} l_{k,i}h_{k,i}(T_i)$ $V_i H_i = \sum_{k=1}^{n} v_{k,i}H_{k,i}(T_i)$ $\sum_{k=1}^{n} S_{kl}^{(T)} l_{kl} = V_i$
6	See Model 5	—	$h_i = \sum_{k=1}^{h} x_{k,i}h_{k,i}(T_i)$ $H_i = \sum_{k=1}^{n} y_{k,i}H_{k,i}(T)$ $\sum_{k=1}^{n} x_{k,i}k_{k,i}(T_i) = 1$

stages. On this basis, all models are classed into those where the enthalpies of the liquid and vapour streams remain constant with column height (see Table III-2, Models 1, 3, 4) and those where the enthalpies vary with height according to the composition of the liquid and vapour streams. The former group may be, and is, used mainly to model the separation of components which only slightly differ in heats of vaporization and, as a consequence, in boiling points. The latter group is used in cases where this difference cannot be neglected, that is, where the components have boiling points spread over a wide range. Failure to allow for changes in the parameters of the





type	vapour composition	type	distillate and reflux composition
1. Partial 2. Total	1. $y_{k,0} = k_{k,0}(T_0)x_{k,0}$ 2. $y_{k,0} = x_{k,0} = x_{k,1}$ $k = 1, \ldots, n$	Total	$y_{k,D} = y_{k,N} = x_{k,N+1}$ $k = 1, \ldots, n$
See Model 3	$y_{k,0} = x_{k,0}(T_0)x_{k,0}$ $y_{k,0} = x_{k,0} = x_{k,1}$ $k = 1, \ldots, n$	See Model 2	1. $y_{k,D} = x_{k,N+1} = y_{k,N}$ 2. $y_{k,D} = y_{k,N}(1-E_D)$ $+ y^*_{k,N+1}(x_{N+1})E_D$ $x_{k,N+1} = \frac{1}{L_{N+1}}(V_N y_{k,N} - D y_{kD})$
Same	1. $\frac{v_{k,0}}{V_0} = k_{k,0}(T)_0 \frac{l_{k,0}}{W}$ 2. $\frac{v_{k,0}}{V_0} = \frac{l_{k,0}}{W} = \frac{l_{k,1}}{L_1}$ $k = 1, \ldots, n$	See Model 3	$\frac{v_{k,D}}{D} = \frac{l_{k,N+1}}{L_{N+1}} = \frac{v_{k,N}}{V_N}$ $k = 1, \ldots, n$
Same	1. $y_{k,0} = x_{k,0}(T_0)x_{k,0}$ 2. $y_{k,0} = x_{k,0} = x_{k,1}$ $k = 1, \ldots, n$	Same	$y_{k,D} = y_{k,N} = x_{k,N+1}$ $k = 1, \ldots, n$

vapour and liquid streams with column height may sometimes lead to gross errors in the calculation of the degree of separation effected by a particular column.

Where calculations are based on the theoretical plate concept, changes in the parameters of the vapour and liquid streams between separation stages are not difficult to take into account, because the compositions are uniquely defined by the equilibrium conditions and the operating line. The situation is different if, in calculating separation, the diffusion mechanism of mass transfer is invoked. While in the separation of closely boiling compo-

nents it is safe to assume an equimolar mass transfer between the liquid and vapour phases, with components widely differing in heats of vaporization, one is forced to reckon with a non-equimolar mass transfer, because of which the compositions at the various stages are not at all easy to determine.

A very important factor governing the operation of rectifying columns near the limit of loading is the entrainment of liquid by vapour from plates. Quantitatively, this is characterized by power functions of vapour velocity. As a rule, the exponent of the power function exceeds three.

It should be noted that failure to take into account liquid entrainment in cases involving the separation of components widely differing in boiling point may lead to major miscalculations in the choice of equipment, as vapour velocity changes considerably with column height. If liquid entrainment markedly changes with height, the miscalculation may result in a reduced efficiency of the column.

So far, we have been examining matters directly related to the modeling of the column proper. A complete model, however, should include partial models representing the reboiler and the condenser.

Existing reboilers may generally be divided into three general types. One is the partial boiler in which heat is supplied by a preheater(s). Another is the total reboiler in which a fraction of the reboiler feed, continually withdrawn from the common feed stream, is vaporized. The third is the live-steam reboiler. While the first type may be treated as an equivalent of an ideal separation stage, the last one is in fact an actual plate with a plate efficiency of less than unity because of short-circuiting. Since a rigorous description of the flow pattern(s) existing in the first and last types of reboiler is a difficult task, it is usual, in modeling, to assume for them the existence of complete mixing.

The condenser may be one of two types, the total condenser (or simply condenser) and the partial condenser (or dephlegmator). In the former case, a mathematical model is based on the assumption that the vapour stream leaving the column and the liquid stream used as reflux have the same composition. If the reflux has a temperature below boiling point, it is important to specify its enthalpy, too.

Generally speaking, a partial condenser ought to be treated as a unit in which mass transfer is accompanied by separation under countercurrent conditions with the continuous condensation of some of the vapour phase. No cases of such an approach to the partial condenser have yet been reported in the literature. Practically, its performance is specified in terms of separation efficiency, as is done for plates. Obviously, this is a very rough approximation to the actual situation, because one can hardly model a partial condenser with a separation efficiency of more than unity. Besides, difficulties arise in the evaluation of the effects that the operating conditions may have on the separation performance of the partial condenser.

As regards the selection of automatic control systems for distillation columns, their dynamic behaviour is a decisive factor. The dynamics of a

control system may in turn be assessed only through the use of models for steady-state conditions.

Modeling algorithms. As previously noted, after a mathematical characterization of a process has been obtained, the next step in the modeling procedure is to solve the equations comprising the mathematical model for a given set of external variables (operating conditions). These external variables are usually chosen to be:

(a) the feed to the column, including the qualitative and quantitative characteristics;

(b) the heat input to the reboiler;

(c) the heat abstracted from the condenser.

The last variable is usually replaced by the characteristics of the reflux, as this makes an analysis of the condenser performance unnecessary.

Some of these external variables may be connected to one another or to the process variables by further relations, and these are then included in the mathematical model when it is used to analyse the associated control system(s).

Mathematically, the design of a complete fractionating plant having a given set of external variables involves solving a system of simultaneous high-order nonlinear equations. The direct methods for its solution known from numerical analysis entail considerable and tedious computations manageable only by high-capacity computers. This is why use is made of methods which utilize the specific features of the equations making up the mathematical model.

In developing an algorithm for solving the equations making up the mathematical model, a good deal depends on whether or not heat balances around column plates are to be taken into account. If heat balances are left out of consideration, the non-linearity of the model equations will mainly be due to the use of expressions for the degree of separation at each stage. Material balances on the unknown compositions are drawn up as linear equations of the form

$$L(x_{i+1,k}-x_{i,k}) = V(y_{i,k}-y_{i-1,k}) \qquad \text{(III-49)}$$

When heat balances around column plates are added to the mathematical model, the liquid and vapour streams in Eqs. (III-49) cannot be treated as specified known terms any longer. Their parameters are now related to the enthalpies of the liquid and vapour phases. Therefore, Eqs. (III-49) become substantially nonlinear

$$L_{i+1}x_{i+1,k}-L_ix_{i,k} = V_{i,k}y_{i,k}-V_{i-1}y_{i-1,k} \qquad \text{(III-50)}$$

In such cases, the model equations are most often solved by an iterative procedure in which the parameters of the material streams and compositions are progressively improved. As a first trial, a fair guess of values for the stream parameters is made, and the compositions are calculated for all stages of separation. Thereafter, the parameters are tested for adequacy. If they are adequate, they are accepted; if not, the procedure is repeated.

Thus, during the calculation of compositions, one solves model equations, except heat balances, with known parameters of the streams in the column. Under the circumstances, an algorithm for solving the model equations that include heat balances may be looked upon as a combination of two algorithms, one concerned with the compositions at the separation stages and the other optimizing the parameters of the vapour and liquid streams in the column. With this approach, a greater proportion of the equations solved at each step is linear, and this removes the difficulty associated with the solution of a system of nonlinear equations.

An algorithm for the calculation of compositions under a given set of vapour and liquid stream parameters may be realized in several ways, based for the most part on the specific properties of the equations that describe the composition distribution among the separation stages.

In one method, calculations are from plate to plate. A major disadvantage of the method is that the flow of calculations tends to become inconsistent, especially when the components being separated differ greatly in volatility. To avoid this, a number of modifications have been proposed, mainly based on the use of different directions of calculation, for example, from the reboiler to the condenser for the heavier components and from the condenser to the reboiler for the lighter components. In another method, calculations start at both ends of the column and work towards the feed plate, that is from the reboiler towards the feed plate, in the stripping section and, from the condenser towards the feed plate in the enriching section. If the two results fail to match at the feed plate, appropriate adjustments are made to the compositions of the products.

With a mathematical model based on the theoretical plate concept under which the vapour composition is assumed to be in equilibrium with the liquid composition on the plate, the balance equations, Eqs. (III-49), become linear in compositions at specified temperatures on the plates. In such cases, the compositions for the separation stages can be computed, using matrix methods applicable to systems of simultaneous linear equations, followed by optimization in the temperature distribution.

In rectification models based on the mechanism of mass transfer, the only method in practical use at present is one in which the calculations are done from plate to plate for the entire column, from the reboiler towards the condenser. If the direction of computation were reversed, one would have to solve a system of transcendental equations for each plate, owing to the structure of the equations describing mass transfer on each plate (see Table III-2, Models 1, 2, and 4). To make the flow of calculations consistent in one direction, efficient algorithms have been developed, which do not call for an appreciable increase in computer capacity and even cut down the machine time in some cases.

Control of a rectifying plant. Rectification is characterized by a number of independent and dependent variables. The independent variables may be divided into two groups, external and internal.

The internal independent variables are the distillate (overhead) composi-

tion, the bottoms product composition, the ratio of the liquid vaporized in the reboiler to the mass flow rate of the feed, the external reflux to distillate ratio. If two of these variables are taken to be independent the remaining two become dependent. This group also includes the compositions and flow rates of vapour and liquid at any column section, the amount of distillate and bottoms product, and the amount of heat removed in the condenser.

In most cases, the automatic control system of a rectifying plant is expected to stabilize the variables governing the process. This type of control is advantageous in cases where the process is subjected to small perturbations and small variations in product quality. Considerable changes in the quantity and composition of the feed entail sustained deviations from the desired quality of the product. Control of a rectifying unit improves as more of the independent variables are stabilized. However, the stabilization of all independent variables, which would eliminate any deviations from the desired heat and material balances in the unit, is unfeasible because of the technical and economic aspects of the rectification process. For example, the composition of the feed usually coming from a previous stage in a given manufacture cannot practically be stabilized, although any change in it may well prove a major disturbing factor for the entire process. Furthermore, since it is sought to admit the feed at boiling point, one has to stabilize the feed temperature.

The feed should be admitted to the column at a constant rate. Therefore, control of feed rate may be regarded as the stabilization of process variables independently of what actually happens in the column. Practically, this can be achieved by using a feed tank to hold a sufficient supply of stock. A suggested arrangement is shown in Fig. III-10.

The composition and boiling point of the liquid on a plate of a rectifying column are closely related to those on any other plate. Any change in them will propagate throughout the column after some time delay. This is why these variables cannot be controlled independently at several points of the column.

The bottoms product is usually discharged by a level controller. The liquid level in the reboiler is related to other controlled variables, namely the temperature (composition) and pressure of the liquid in the column. Depending on the physical properties of the feed, reboiler design, the thermal load on the reboiler and some other factors, the extent of interrelationships between the variables may be widely different. If the interrelationship is loose, one may well use level regulation (see Fig. III-10).

It will be advantageous to stabilize the flow rate of heating steam only if the feed has constant composition. If the feed composition is a varying quantity, an attempt to maintain a constant rate for heating steam would bring about considerable variations in the composition of the bottoms product, which is undesirable. The mass flow rate of feed should likewise be constant, since otherwise a decrease in the feed rate, with the steam rate held constant, would cause the column temperature to rise, thereby impair-

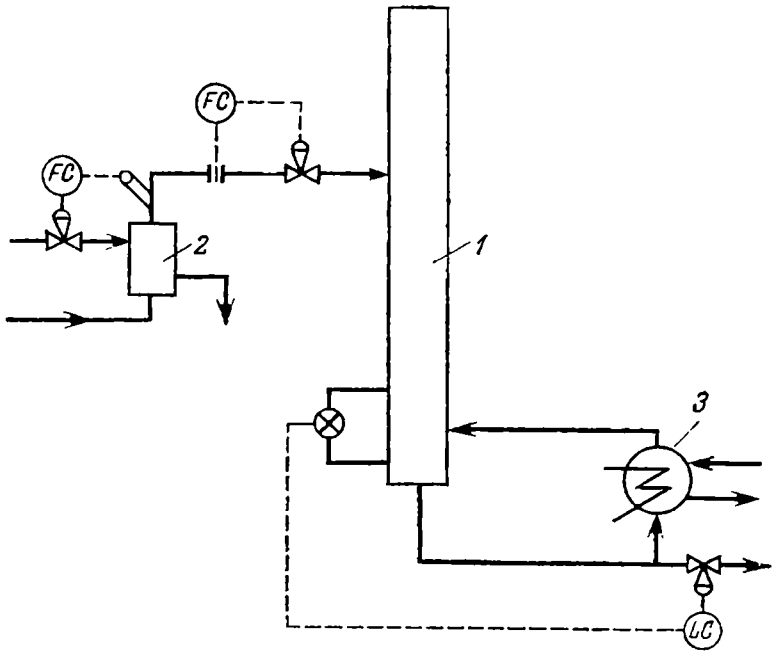


Fig. III-10. Feed and reboiler-level control system
1 — column; *2* — preheater; *3* — reboiler; *FC* — flow-rate controller; *LC* — level controller

ing the purity of the distillate. With an increase in the feed rate, some of the low boiler may find its way into the bottoms product.

The distillate (overhead) product is usually withdrawn from an accumulator. Variations in its level usually have no effect on the rectification process. Under the circumstances, level control of the accumulator may be treated as a task in its own right and with no connections to the main process.

The correct functioning of a rectifying unit depends on the quality of column pressure control. This is especially true of cases where the feed consists of closely boiling components.

A system for the separate control of pressure in the column and the accumulator is shown in the diagram of Fig. III-11. This arrangement ensures operation of the condenser under constant conditions and a uniform flow rate of condensate into the accumulator.

Ratio control systems. In the control of product quality, the most troublesome disturbances are changes in the mass flow rate and composition of the feed. As follows from an overall material balance around the distillation unit, the flow rate of only one product stream can be adjusted at will. The flow rate of the other product will then be decided by the feed rate and is therefore a dependent variable. Thus, the flow rate of either the distillate or of the bottoms product may be chosen to be manipulated, directly or indirectly, by the control system. However, the distillate to steam ratio should be maintained constant so as not to impair the separating performance of the unit.

With column pressure held constant, a ratio control system may be realised basically in two ways:

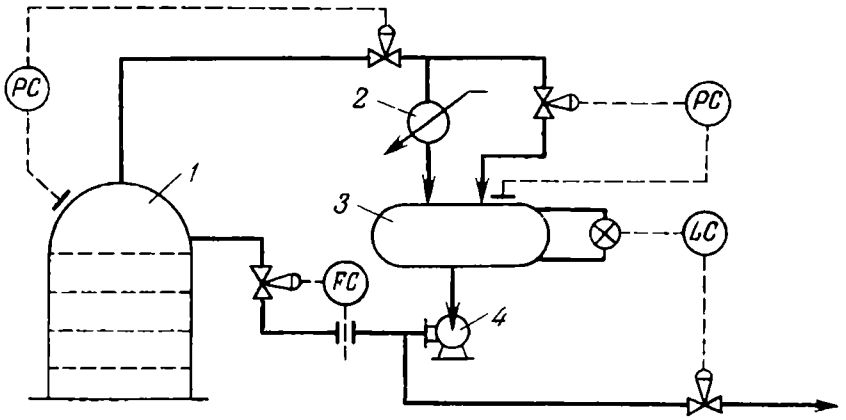


Fig. III-11. Separate control for column and accumulator pressure
1 — column; *2* — condenser; *3* — accumulator; *4* — pump; *PC* — pressure controller; *LC* — level controller; *FC* — flow rate controller

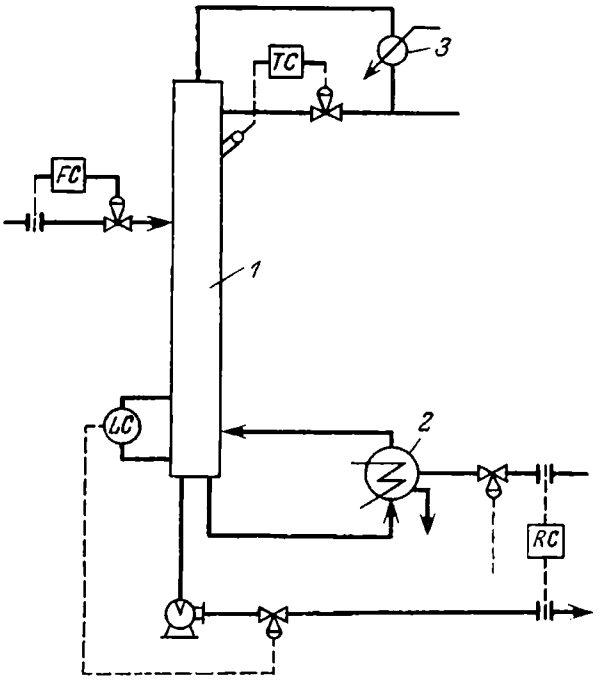


Fig. III-12. Distillate-to-steam ratio control
1 — column; *2* — reboiler; *3* — condenser

1. Control to maintain the flow of distillate in a fixed ratio to the flow of heating steam to the reboiler (Fig. III-12). A level controller, *LC*, maintains the level and controls the flow rate of the bottoms product. A ratio controller, *RC*, controls the flow of heating steam to the reboiler so that it is held in a fixed ratio. The reflux flow rate is controlled by a temperature controller, *TC*, according to the temperature at the column top.

2. Control to maintain a constant reflux ratio (Fig. III-13). A level controller, *LC*, maintains the bottoms product at a constant level, and a ratio

controller, *RC*, maintains a constant reflux ratio. The flow of steam to the reboiler is controlled by a flow controller, *FC*, according to the temperature at the bottom of the column.

The above configurations can readily be instrumented and are mainly applicable to binary mixtures. For feeds containing more than two components, it is important that the temperature at the sampling point bear a univalued relation to the mixture composition.

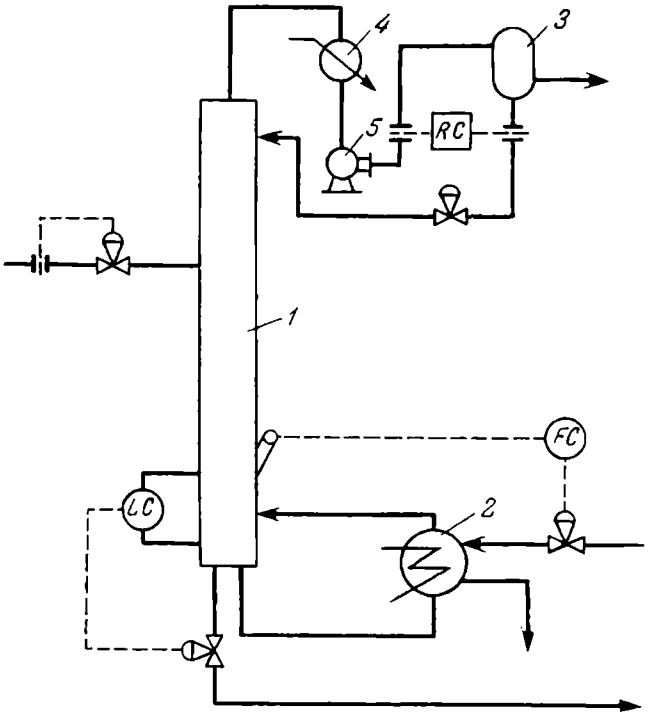


Fig. III-13. Fixed reflux ratio control
1 — column; *2* — reboiler; *3* — accumulator; *4* — condenser; *5* — pump

The configuration of Fig. III-12 is most often used in cases where the requirements for the quality of the bottoms product are of primary importance, and that of Fig. III-13 where the same applies to the quality of the distillate (top product).

Among the demerits of ratio control systems are the following:

1. The reflux ratio may be increased (or the amount of top product drawn off may be decreased) excessively, thereby cutting down the throughput of the unit. Alternatively, the reflux ratio may be decreased (and the amount of top product drawn off may be increased), thereby impairing the separating performance of the column. One way to avoid a reduction in the performance is to adjust the ratio of heating steam to the bottoms product or the reflux ratio with a margin such that the performance will remain at the requisite level despite the most adverse characteristics of the feed. However, the unit will operate uneconomically at average parameters. Thus, one has to seek a compromise between economic performance and reliability.

2. The choice of a plate from which a signal for control of the reflux ratio can be taken is a fairly complicated problem.

Feedforward control systems. Control under conditions of variations in the mass flow rate and composition of the feed may be realized as feedforward control in any one of two ways, namely: as control of distillate flow or as control of heat input to the reboiler. In some cases, both arrangements may be used together.

Feedforward control involves a continuous solution of a material balance equation in the course of operation:

$$P = F\frac{x_F - x_W}{y_p - x_W}$$

where P is the flow of distillate, F is the flow of feed, x_F is the feed composition, y_p is the overhead vapour composition, and x_W is the bottoms composition.

In addition to sensing and final control elements, an automatic control system also contains computing elements which supply the requisite control actions. The relationships utilized by the computing elements are specified in advance on the basis of performance analysis.

An overhead and bottom composition control system (Fig. III-14) consists of two control loops. One loop maintains the flow of feed in a fixed ratio to the flow of distillate or secures the desired top product draw-off according to the material balance. At a constant performance of the unit,

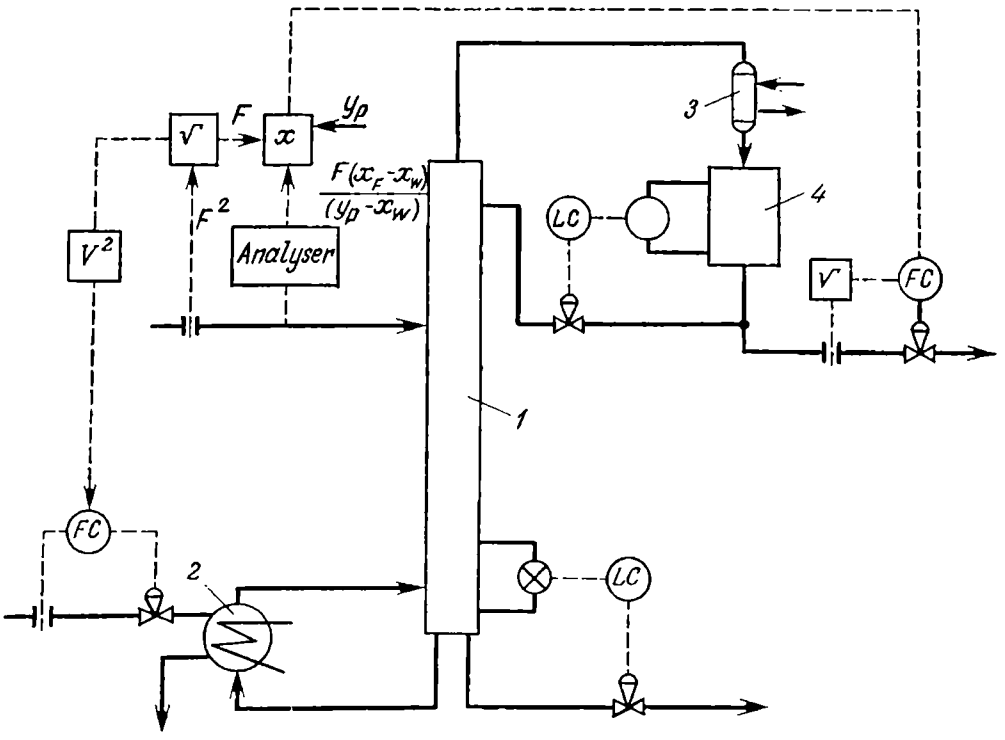


Fig. III-14. Feedforward control

1 — column; *2* — reboiler; *3* — condenser; *4* — accumulator

the flow rate of distillate is directly proportional to the component content of the feed. Since the low-boiling content of the feed depends on the feed flow and composition, the feed line has, in addition to a flow transmitter, a composition analyser. Signals from the flow transmitter and the composition analyser are operated upon by an arithmetic unit which calculates the ratio and finds how far it has deviated from the set point. This is done by extracting the square root, $\sqrt{}$, and raising to the square, V^2.

The second loop maintains the mass flow rate of feed in a fixed ratio to the flow of heating steam to the reboiler. The actuators in both loops are flow controllers, *FC*.

In an overhead and bottom composition control system, the separating performance may be maintained constant by manipulating the ratio of the heating steam flow to the mass flow rate of feed. In such a case, the flow of the top product need be adjusted only when a change occurs in the feed composition.

A change in the feed composition brings about a change in feed enthalpy. This, too, may serve as a basis for feed forward control. The point is that a change in feed enthalpy changes the relative quantities of distillate and bottoms product. The control system may be arranged so that the flow of vapour at the top will be maintained constant (as a consequence, the distillate composition will likewise remain constant), while the quality of the bottoms product will be changed.

A feedforward control system always contains a greater number of components than a feedback system. Among the advantages of feedforward control are an increased yield of product owing to a cut-down in flow rate coefficients, a reduced energy consumption, and a reduction in the capacity of intermediate tanks or accumulators.

(C) LIQUID-LIQUID EXTRACTION IN PACKED TOWERS

The form of mathematical model for a liquid extraction tower is selected according to the flow pattern(s) prevailing under a given set of operating conditions. In fact, the flow pattern decides all the basic parameters of the process model, including the direction and velocity of the streams in the tower, hold-up, and the rate of mass transport across the interface.

The limits for the various flow patterns are as follows: a free flow of droplets at $w_d/w_c < 0.15$, a constrained flow of droplets at $w_d/w_c \approx 0.15$ to 1, where w_d is the velocity of the dispersed phase, and w_c is the velocity of the continuous phase, or the flooding velocity.

The velocity of the continuous phase, w_c, at flooding is given by[5]

$$\log_{10}\left[\frac{w_c^2 a \gamma_c}{g F_v^3 \Delta\gamma}\mu_c^{0.16}\left(\frac{\sigma_{cd}}{\sigma_{ca}-\sigma_{da}}\right)^{0.2}\right] = -0.474 - 1.75(V_d/V_c)^{1/4}(\gamma_c/\gamma_d)^{1/8} \quad \text{(III-51)}$$

where a is the specific surface area of packing, F_v is the fraction void o packing, γ_c and γ_d are the specific weights of the continuous and dispersed phases, μ_c is the viscosity of the continuous phase, V_c and V_d are the space

(volume) velocities of the continuous and dispersed phases, σ_{cd} is the interfacial tension, σ_{ca} and σ_{da} are the surface tensions of the liquids.

The linear velocities of the phases can be found by the equation

$$w_d = w_c(V_d/V_c) \tag{III-52}$$

The dispersed phase hold-up of the tower, h_d, under various load conditions may be found approximately from the equation

$$V_d/h_d + V_c/(1-h_d) = F_v V_0(1-h_d) \tag{III-53}$$

where V_0 is the average velocity of rise for droplets of the dispersed phase inside the packing, assuming a stationary continuous phase, that is, at $V_c = 0$ and at $V_d \to 0$ (the value of V_0 is found by experiment).

Plug-flow model. For this model we have:

$$w_c \frac{\partial c_c}{\partial l} - (K_V)_c(c_c - c_c^*) = 0 \tag{III-54}$$

$$w_d \frac{\partial c_d}{\partial l} + (K_V)_d(c_d^* - c_d) = 0$$

Dispersion model. For this model we have:

$$D_c \frac{\partial^2 c_c}{\partial l^2} - w_c \frac{\partial c_c}{\partial l} - (K_V)_c(c_c - c_c^*) = 0$$

$$D_d \frac{\partial^2 c_d}{\partial l^2} + w_d \frac{\partial c_d}{\partial l} + (K_V)_d(c_d^* - c_d) = 0 \tag{III-55}$$

In calculations, it is assumed that the coefficient of mass transfer remains unchanged with tower height, while the linear stream velocities, w_d and w_c, and the longitudinal dispersion numbers, D_c and D_d, remain constant with height and over cross-section.

Equations (III-54) and (III-55) are solved on digital computers. The coefficients of mass transfer, $(K_V)_c$ and $(K_V)_d$, the longitudinal dispersion numbers, D_c and D_d, and the linear stream velocities, w_c and w_d, entering Eqs. (III-54) and (III-55) are found by experiment.

Recently, more adequate models for packed extraction towers have been developed, a cascade model with backmixing[6] and a cascade model with stagnation regions.[7]

III-3. USE OF MECHANICAL AGITATORS FOR LIQUID MEDIA

Mixing in stirred-tank reactors has received considerable attention in the literature. The investigators have studied the effect of the rotational speed, configuration and location of agitators, the number and form of baffles or partitions, the physico-chemical properties of the medium, the location of stream inlets and outlets, and a number of other factors. Unfortunately, there are cases where these findings cannot be applied directly because each process has features specific only to it. As a result, stirred-tank reactors are

still designed by trial and error, the processes in them fail to approach the ideal, and reactor performance turns out to be sub-standard. Under the circumstances, it is highly desirable that a model be developed that would be common to a sufficient number of situations and, at the same time, readily adaptable to particular conditions.

In reactors using a paddle agitator, there is a radial flow pattern which divides into two currents at the walls. The magnitudes of these currents depend on the location of the agitator which partitions the reactor into a top and a bottom region, each with a circulatory pattern of its own. This reactor flow pattern can conveniently be approximated by a variable-pattern, recycle model[8] made up of two recycle circuits with a variable number of well-stirred stages in each, merging together at the agitator region which is a well-stirred stage, too. The controlling factor of the model is the inlet-stream path coincident with the paths of the circulatory currents in the reactor and depends on the relative position of the inlets and outlets. The volume of the regions in each circuit depends on the location of the agitator and may be found by the following equations:

the volume of the region above the agitator

$$V_a = \frac{\pi D^2}{4}(H-h) - \frac{V_m}{2} \tag{III-56}$$

the volume of the region under the agitator

$$V_b = \frac{\pi D^2}{4}h - \frac{V_m}{2} \tag{III-57}$$

where H is the level of the liquid in the reactor, h is the distance from the reactor to the paddle agitator, and D is the reactor diameter.

The volume of the complete-mixing region around the agitator is given by

$$V_m = \frac{\pi b}{12}(5D^2 + d^2 + Dd) \tag{III-58}$$

where d is the diameter of the circle swept by the agitator paddle.

The number of stages in the top and bottom regions may be found from the relation

$$\nu = n_l/n_s \tag{III-59}$$

Changes in the location of the agitator will strain the model as follows:

$$\left.\begin{array}{llll} n_a = n_s = 1 & n_b = n_l = \nu & \text{at } h/H > 0.5 \\ n_a = n_b = 1 & & \text{at } h/H = 0.5 \\ n_a = n_l = \nu & n_b = n_s = 1 & \text{at } h/H < 0.5 \end{array}\right\} \tag{III-60}$$

where n_l is the number of stages in the larger region, n_s is the number of stages in the smaller region, n_a is the number of stages in the region above the agitator, and n_b is the number of stages in the region below the agitator. In all of these cases, the smaller region has one stage ($n_s = 1$).

The total volumetric flow, q, is given by

$$q = q_1 + q_2 = 1.535\, d^2 b\omega \qquad \text{(III-61)}$$

where q_1 is the volumetric flow in the top circuit, q_2 is the volumetric flow in the bottom circuit, b is the paddle width, and ω is the rpm of the agitator.

With sufficient accuracy, the relationship between the flows in the top and bottom circuits may be described by the following expression

$$q_1/q_2 = h/(H-h) \qquad \text{(III-62)}$$

The inlets into, and outlets from, the reactor are located on the opposite sides of the reactor's circumference (Fig. III-15). This arrangement of inlets and outlets governs the path of the inlet stream.

In most cases, models are analysed in terms of their transfer functions, or the ratio of the transform of the output to the transform of the input. However, any change in the location of the inlet and outlet will immediately affect the transfer function, and an analysis on the basis of transfer functions becomes unfeasible. Instead, we shall work on the assumption that the models of interest are Markov processes. An example of the validity of such an assumption is given below.

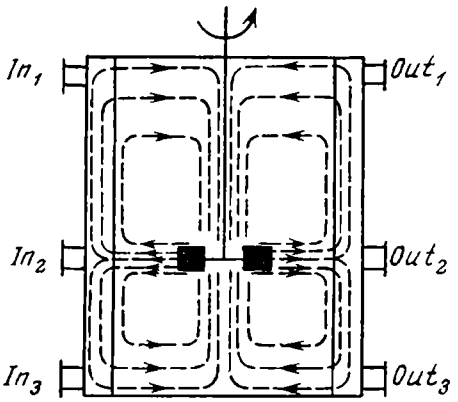


Fig. III-15. Flow pattern in a stirred tank with a paddle agitator

Let a system have $N-1$ well-stirred stages interconnected by known flows. Designating the system outlet as N, we shall find the volume of the kth stage as V_k, and the volumetric flow from the kth to the jth stage as q_{kj}. Let us label a fluid element in the system and define the state of the system with a vector, $E(n)$, where $n = 0, 1, 2, \ldots$ with coordinates $e_k(n)$ describing the probability of finding the labelled fluid element in the kth stage after n passes, such that

$$\sum_{k=1}^{N} e_k(n) = 1 \qquad \text{(III-63)}$$

Over a small time interval, $\Delta\tau$, the tracer element may either remain in a stage or pass into another. We choose $\Delta\tau$ to be such that the tracer fluid element will pass into an adjacent stage, but will not be able to pass through it, and also such that this transition may be treated as an instantaneous one. The behaviour of a fluid element in such a system may be described in terms of Markov processes, that is, the probability of finding the fluid element in the kth stage after $n+1$ passes will be solely determined by the probability of finding it in the jth stage after n passes and by the probability p_{jk} that the fluid element will pass from the jth to the kth stage. Therefore,

we may write

$$e_k(n+1) = \sum_{j=1}^{N} e_j(n)p_{jk} \tag{III-64}$$

The probabilities p_{jk} may be arranged in a transition probability matrix

$$P = \begin{vmatrix} p_{11} & p_{12} & p_{13}, \ldots, p_{1N} \\ p_{21} & p_{22} & \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots & p_{NN} \end{vmatrix} \tag{III-65}$$

Matrix (III-65) is a stochastic matrix and, together with the initial distribution $E(0)$, fully defines the state of the system after n transitions, which may be found by the equations

$$\left.\begin{aligned} E(1) &= E(0)P \\ E(2) &= E(1)P \\ &\ldots\ldots\ldots\ldots \\ E(n+1) &= E(n)P \end{aligned}\right\} \tag{III-66}$$

where $E(0)$, $E(1)$, $E(2)$, ..., $E(n)$ are the states of the system after a time interval equal to 0, $\Delta\tau$, $2\Delta\tau$, ..., $n\Delta\tau$.

Since a fluid element leaving the system cannot enter it again, we also have

$$P_{NN} = 1 \quad P_{Nk} = 0 \quad (\text{at } k \neq N) \tag{III-67}$$

Thus, what we have is a typical absorbing Markov chain, or a random walk. In our case, the absorbing barrier is the system outlet, N.

The elements p_{kk} of the stochastic matrix P are equal to the probability that in time $\Delta\tau$ the fluid element will not leave the kth stage. Then, assuming that the probability distribution is exponential for each stage, we may write

$$p_{kk} = \exp\left(-\frac{\sum\limits_{\substack{k=1 \\ j\neq k}}^{N} q_{jk}}{V_k}\Delta\tau\right) \tag{III-68}$$

where $k = 1, 2, \ldots, N-1$.

The remaining matrix elements can be found by the equation

$$p_{kj} = \frac{q_{kj}}{\sum\limits_{\substack{k=1 \\ j\neq k}}^{N} q_{jk}}\left[1-\exp\left(-\frac{\sum\limits_{\substack{k=1 \\ j\neq k}}^{N} q_{jk}}{V_k}\Delta\tau\right)\right] \tag{III-69}$$

where $k = 1, 2, \ldots, N$; $j = 1, 2, \ldots, N-1$.

It is an easy matter to see that the sum of elements in each row is equal to unity

$$\sum_{k=1}^{N} p_{jk} = 1 \tag{III-70}$$

where $j = 1, 2, \ldots, N$.

The initial state probability vector, $E(0)$, is determined by the inlet stream, and its coordinates are equal to the probabilities of finding the tracer (labelled) fluid element in each stage at time $\tau = 0$.

Using Eq. (III-67) repeatedly n times, we shall find the state of the system at any time τ. The vector $E(n)$ describes the residence time distribution for the system. The coordinate $e_k(n)$ of the vector $E(n)$ represents the residence time distribution for the kth stage, and $e_k(n)\,\Delta\tau$ is the probability that the fluid element will remain in the kth stage between time $(n-1)\Delta\tau$ and $n\Delta\tau$, that is, it is the response of the kth stage to an impulse stimulus. The coordinate $e_{N-1}(n)$ applies to the residence time distribution for the entire system, and the coordinate $e_N(n)$ applies to the probability that the tracer fluid element will leave the system in a time $n\Delta\tau$, and is therefore the integral of the residence time distribution or the response of the system to a step stimulus:

$$e_N(n) = \sum_{n=0}^{N} e_{N-1}(n)\,\Delta\tau \tag{III-71}$$

Thus, we can find two basic characteristics of the process, namely the residence time distribution density or the C-diagram, and the integral of the residence time distribution, or the F-diagram. From these diagrams, we can readily determine the average residence time for the system and the sample variance of the distribution about the mean (that is, the first and second moments of the distribution):

$$\tau_n = M_1 \frac{\sum_{n=1}^{\infty} e_{N-1}(n)n}{\sum_{n=1}^{\infty} e_{N-1}(n)}\,\Delta\tau = \sum_{n=1}^{\infty} [1 - e_N(n)]\,\Delta\tau \tag{III-72}$$

$$s^2 = M_2 = \sum_{n=1}^{\infty} (n\Delta\tau - M_1)^2 e_{N-1}(n) = 2\sum_{n=1}^{\infty} [1 - e_N(n)]n\,\Delta\tau - \left\{\sum_{n=1}^{\infty} [1 - e_N(n)]\,\Delta\tau\right\}^2 \tag{III-73}$$

and also the intensity function, λ, which is characteristic of imperfect-mixing processes:

$$\lambda(n) = \frac{e_{N-1}(n)}{1 - e_N(n)} \tag{III-74}$$

As an example, we shall develop a transition probability matrix and an initial state matrix for $h/H = 0.8$ and for the feed stream whose path is decided by the inlet and outlet ports, In_1 through Out_3 shown in Fig. III-15.

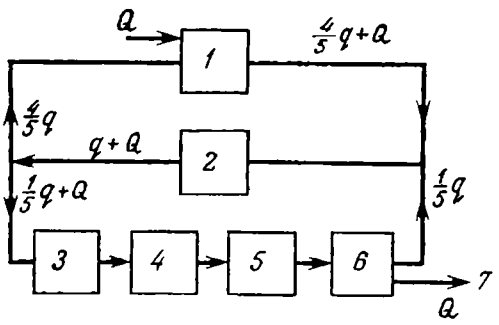


Fig. III-16. Two-circuit recycle stirred-tank model for $h/H = 0.8$ and $In_1 = Out_3$

The volume of the complete mixing region around the agitator can be found by Eq. (III-58). Then, using Eqs. (III-56) and (III-57), we find the volumes of the top and bottom regions. The ratio of the larger (bottom) to the smaller (top) volume is approximately

$$\nu \approx \frac{h/H}{1-h/H} = 4$$

Hence, using Eq. (III-60), we get: $n_a = 1$, $n_b = 4$ (Fig. III-16). In time $\Delta\tau$, the tracer fluid element will either remain in stage 1 or will pass into stage 2. The probabilities of these events respectively are

$$p_{11} = \exp\left(-\frac{q_1+Q}{V_a}\Delta\tau\right)$$

$$p_{12} = \left[1-\exp\left(-\frac{q_1+Q}{V_a}\Delta\tau\right)\right]$$

where Q is the volumetric flow through the reactor. The probability of transitions to other stages is zero in this case. Then the tracer fluid element may either remain in stage 2 or pass into stage 1 or 3. The respective probabilities are

$$p_{22} = \exp\left(-\frac{q+Q}{V_m}\Delta\tau\right)$$

$$p_{21} = \frac{q_1}{q+Q}\left[1-\exp\left(-\frac{q+Q}{V}\Delta\tau\right)\right]$$

$$p_{23} = \frac{q_2+Q}{q+Q}\left[1-\exp\left(-\frac{q+Q}{V}\Delta\tau\right)\right]$$

The succeeding path of the tracer element may be followed in a similar way. Let $V_m = 0.1V$, where V is the volume of the liquid in the reactor. Substituting the values of h/H and V_m in Eqs. (III-56) and (III-57), we find $V_a = 0.18\ V$ and $V_b = 0.72\ V$. Using Eqs. (III-61) and (III-62), we find the volumetric flows for the top and bottom circuits: $q_1 = 0.8\ q$ and $q_2 = 0.2\ q$.

Now, the transition probabilities may be written as follows:

$$p_{11} = \exp\left(-\frac{0.8q/Q+1}{0.18}\Delta T\right)$$

$$p_{21} = \frac{0.8q/Q}{q/Q+1}\{1-\exp[-10(q/Q+1)\Delta T]\} \text{ etc.}$$

where

$$\Delta T = \Delta\tau\frac{Q}{V}$$

Next, we may compile the transition probability matrix

$$P = \begin{bmatrix} \exp x & (1-\exp x) & 0 & 0 & 0 & 0 & 0 \\ \left[\frac{0.8q/Q}{q/Q+1}(1-\exp y)\right]\exp y & \left[\frac{0.2q/Q+1}{q/Q+1}(1-\exp y)\right] & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \exp z(1-\exp z) & & & & \\ 0 & 0 & 0 & \exp z(1-\exp z) & & 0 & 0 \\ 0 & 0 & 0 & 0 & \exp z(1-\exp z) & & 0 \\ 0 & \left[\frac{q/Q}{q/Q+5}(1-\exp z)\right] & 0 & 0 & 0 & \exp z\left[\frac{5}{q/Q+5}(1-\exp z)\right] & \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

where

$$x = \left(-\frac{0.8q/Q+1}{0.18}\Delta T\right)$$

$$y = [-10(q/Q+1)\Delta T]$$

$$z = \frac{0.2q/Q+1}{0.18}\Delta T)$$

and q/Q is the ratio of the circulatory flow to the total flow.

The initial state probability vector is $E(0) = [1, 0, 0, 0, 0, 0, 0]$, because at $\tau = 0$, the tracer fluid element enters the stage l, and the probability of finding it in any other stage is zero. Knowing P and $F(0)$, we can find the state of the system at any time τ by Eq. (III-66).

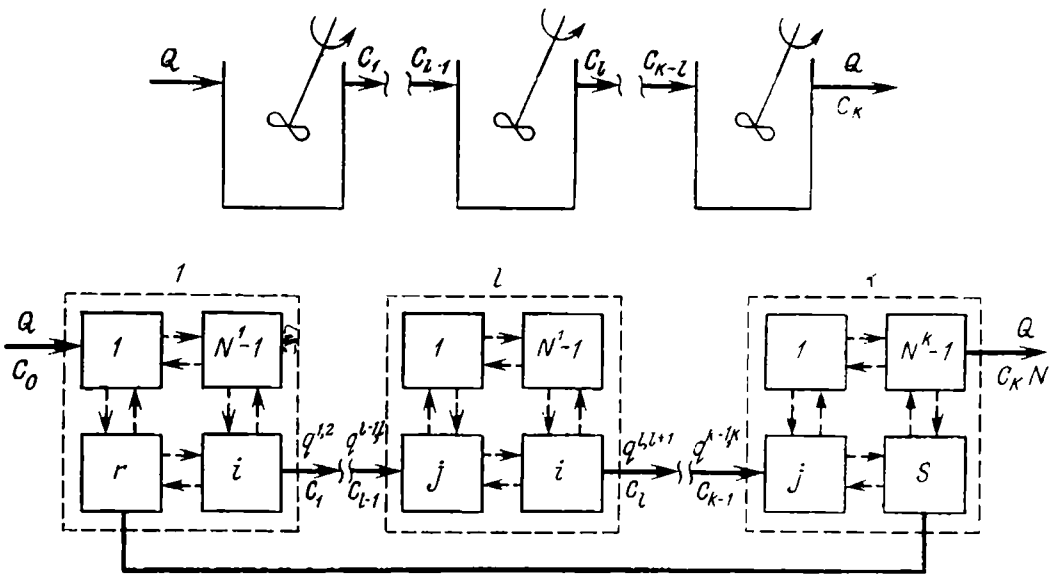


Fig. III-17. Cascade of incomplete mixers

Cascade of imperfectly mixed tanks. Stochastic model.[9] Using a stochastic model of a single imperfect mixer, a cascade of such mixers may be represented as an integral complex topologic structure consisting of all the stages in each mixer, interconnected by both the flows within each mixer, and by the streams between the mixers (Fig. III-17). With this presentation, it is an easy matter to take account of the effects produced by the recycle and bypass streams, which enter the matrix P as additional elements.

Let $N-1$ be the number of well-stirred stages in all the mixers of the cascade. For a cascade of identical reactors, this number will be

$$N-1 = (N^l-1)k \qquad \text{(III-75)}$$

and for a cascade of nonidentical reactors it will be

$$N-1 = \sum_{l=1}^{K}(N^l-1) \qquad \text{(III-76)}$$

where N^l is the number of well-stirred stages in the lth mixer.

Designating the cascade outlet as N, the initial state vector $E(0)$ will be of the Nth order, with its coordinates representing the distribution of the feed stream among the reactors and the location of the inlet to each reactor. Besides, we may write an (N by N) matrix P of the form

$$P = \begin{vmatrix} p^{1,1}\, p^{l,2} & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & p^{l,l} & p^{l,l+1} & \cdots \\ \cdots & \cdots & p^{l+1,l+1} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ p^{k,1} & \cdots & p^{k,k} & p^{k,N} \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & 0 & p^{N,N} & \cdots \end{vmatrix} \qquad \text{(III-77)}$$

In this matrix, the $p^{l,l}$ elements in turn make up a stochastic matrix similar to (III-65) for the lth mixer. The element $p^{k,N}$ is a column vector containing the $p_{i,N}^{k,N}$ term which is the probability that the tracer fluid element will pass from the ith stage on to the outlet. The element $p^{l,l+1}$ is a matrix containing one term, $p_{i,j}^{l,l+1}$, which is the probability that the tracer fluid element will pass from the ith stage of the lth mixer to the jth stage of the $(l+1)$ mixer. The element $p^{k,1}$ is a matrix containing one term, $p_{s,r}^{k,1}$, which is the probability that the tracer fluid element from the sth stage of the last mixer will pass into the rth stage of the first mixer, that is, the recycle.

Since the tracer fluid element may reach the outlet of only the last mixer, the elements in the last column, except $p_{i,N}^{k,N}$ and $p^{N,N}$, will be equal to zero. Furthermore, the tracer fluid element reaching the outlet cannot enter the system again, and so all elements in the last row, except $p^{N,N}$, in the matrix of (III-77), will be equal to zero, and $p^{N,N} = 1$.

The behaviour of the tracer fluid element in such a system is described by a recursion relation of the form

$$E(n+1) = E(n)P \qquad \text{(III-78)}$$

Thus, the algorithm for stage computation remains the same, and only the order of the matrix and, as a consequence, that of the row vector is raised. To state this differently, the equations describing the residence time distribution in a single mixer derived earlier remain in force.

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CHAPTER IV

MATHEMATICAL MODELS OF CHEMICAL REACTORS

Mathematical models of chemical reactors are based on the flow-pattern models discussed earlier. In them, account is taken of the residence time distribution of fluid elements in the reactant stream in a given reactor and also equations of chemical kinetics.[1, 2]

IV-1. BASIC CONCEPTS OF CHEMICAL KINETICS

Rate of a chemical reaction. Sometimes called the reaction velocity, this quantity describes the change (decrease or increase) in the number of moles of the reactants due to a chemical interaction per unit time per unit volume (for homogeneous reactions) or per unit surface area or mass (for heterogeneous reactions).

Accordingly, the rate of homogeneous reactions is given by

$$w_r = \frac{1}{V} \cdot \frac{dN}{d\tau} \quad \frac{\text{moles of product}}{\text{(liquid volume) (time)}} \tag{IV-1}$$

According to Eq. (IV-1) and introducing the concentration, c, we obtain in the general case

$$w_r = \frac{1}{V} \cdot \frac{d(cV)}{d\tau} = \frac{1}{V} \frac{V\,dc + c\,dV}{d\tau} \tag{IV-2}$$

or

$$w_r = dc/d\tau + (c/V)\,(dV/d\tau) \tag{IV-3}$$

For reactions proceeding in a closed constant-volume system, the second term in Eq. (IV-3) is equal to zero, and the equation reduces to the form

$$w_r = \pm dc/d\tau \tag{IV-4}$$

The "+" sign indicates that the reaction leads to an accumulation of the substance. The "−" sign indicates that the substance is depleted.

For heterogeneous reactions the reaction rate may be defined by

$$w_r = \frac{1}{S}\frac{dN}{d\tau}\frac{\text{moles of product}}{\text{(area) (time)}} \tag{IV-5}$$

$$w_r = \frac{1}{G}\frac{dN}{d\tau}\frac{\text{moles of product}}{\text{(mass) (time)}} \tag{IV-6}$$

According to the law of mass action, the reaction rate is proportional to the current concentration of the reactants. Then, for a reaction between original components A and B, we shall have

$$w_r = kc_Ac_B \tag{IV-7}$$

where k is a proportionality constant, variously called the specific reaction rate, reaction constant, velocity constant, or rate coefficient.

Specific reaction rate. This quantity has the units of the specific reaction and of concentration:

$$[k] = [w_r/c] = \left[\frac{\text{moles} \times \text{litres}}{\text{litres} \times \text{seconds} \times \text{moles}}\right] = [s^{-1}]$$

The specific reaction rate applies to processes which take place at the molecular level and, like any molecular relationship, it depends on the kinds of molecules involved, and on temperature. For a given kind of molecules, k = constant.

In 1889, Arrhenius proposed what is known now as the Arrhenius equation:

$$k = k_0e^{-E/RT} \tag{IV-8}$$

where k_0 is the pre-exponential factor or the frequency factor which is the collision number for biomolecular reactions; E is the activation energy, kJ/kmole (kcal/kmole); R is the universal gas constant, kJ kmole^{-1}/deg^{-1}; T is the absolute temperature, °K; and E/RT is a dimensionless parameter.

Molecularity. The molecularity describes the number of molecules participating in a reaction in accordance with its stoichiometric equation and must be an integer. There are reactions with a molecularity of one (monomolecular), two (biomolecular) and (seldom) three (trimolecular). A reaction will be an elementary one if it takes place through one step and there is a concordance between the stoichiometric and rate equations. If there is no concordance, the reaction is not elementary.

Reaction order. The manner in which the rate of a chemical reaction is controlled by the concentration of each reactant is specified as a power exponent of that reactant's concentration, and this is the reaction order with respect to that particular reactant. With several reactants, the overall reaction order is the sum of the power exponents of the reactants. Furthermore, the reaction order is proportional to the reactant's concentration in the case of a first-order reaction, to the product of the concentrations of two reactants for a second-order reaction, to the product of the concentrations of three reactants for a third-order reaction, etc.

The molecularity and the order of the same reaction may or may not be equal. This is because a given reaction may be a sequence of several steps each occurring at a different rate (in which case the reaction may have a fractional order) or because there is a great difference in concentration. For example, a first-order reaction may have a molecularity of one ($A \rightarrow R+S$) or of two ($A+B \rightarrow R+S$). In the latter case, there is a large excess of one reactant, say B, and its concentration remains practically constant during the reaction.

When the mechanism of the reaction is unknown, the reaction rate for several reactants may be approximated by the following expression

$$w_r = kc_A^a c_B^b, \ldots, c_P^p = kc_A^n \qquad \text{(IV-9)}$$

where a is the reaction order with respect to A, b is the reaction order with respect to B, p is the reaction order with respect to P, and $a+b+\ldots+p = n$ is the overall reaction order.

As already noted, the reaction order may be an integer or a fraction, and is found by experiment, while the molecularity must always be an integer.

Limiting reactant. In developing a mathematical model for a process with a chemical reaction, one has in the general case to describe the changes that each of the reactant undergoes. Then for complex reactions, the number of equations might rise to a point where the model would hardly be convenient for use in analysis of the process.

The number of such equations may be reduced to an acceptable minimum by using only those for so-called *limiting reactants*. Then the behaviour of the remaining reactants may be described by simple stoichiometric equations expressed in terms of the concentrations of the limiting reactants.

For simple cases, such as $A \rightarrow B$, the choice of the limiting reactant is simple, because either A or B may be chosen. If A be the limiting reactant the concentration of B will be uniquely defined at any instant by

$$c_B = c_{A0} + c_{B0} - c_A \qquad \text{(IV-10)}$$

where c_{A0} and c_{B0} are the initial concentrations of A and B, c_A is the current concentration of A found with allowance for the specific mechanism of the reaction.

In the case of complex chemical reactions, the choice of limiting reactant becomes complicated and, in some cases, no longer univalued. This is why one has to resort to a set of well-defined rules.

As an illustration of these rules, we shall examine a reaction proceeding to the scheme

$$\left.\begin{aligned} \alpha_1 A + \beta_1 B &\rightleftarrows \gamma_1 C \\ \gamma_2 C + \beta_2 B &\rightleftarrows \delta D \end{aligned}\right\} \qquad \text{(IV-11)}$$

where α, β, γ, and δ are the respective stoichiometric coefficients.

To simplify the discussion, we shall introduce the concept of a *reaction step*. This will be understood as an elementary chemical change applying

only to the reactants directly involved. Then, the reactions $\alpha A \rightleftarrows \beta B$ and $\alpha A \rightarrow \beta B \rightarrow \gamma C + \delta D$ should be treated as those made up of two steps:

$$\alpha A \rightarrow \beta B \quad \text{and} \quad \beta B \rightarrow \alpha A$$
$$\alpha A \rightarrow \beta B \quad \text{and} \quad \beta B \rightarrow \gamma C + \delta D$$

The rate (or velocity) of a reaction step is defined by the rate (or velocity) of change of any reactant or product involved in that step divided by the respective stoichiometric coefficient. For the reactants, the stoichiometric coefficients will be taken with a "minus" sign, and for the products with a "plus" sign. Then the rate of a reaction step will always be a positive quantity, irrespective of the reactant or product with respect to which it has been found.

As a proof, let for an elementary reaction, $\alpha A \rightarrow \beta B$, the rate of change, expressed in kmole $m^{-3}\ s^{-1}$, be w_{rA} and w_{rB} and also let w_{rA} be negative. Now the rate of a reaction step defined by

$$r = w_{rA}/-\alpha = w_{rB}/\beta$$

will always be positive and always the same, irrespective of the reactant for which it has been determined. This is because for the above reaction the relation

$$w_{rB} = -\frac{\beta}{\alpha} w_{rA}$$

holds always.

Similarly, it may be shown that the rate of a reaction step can be defined as above, using the rate of change of any reactant or product in the reaction $\alpha A + \beta B \rightarrow \gamma C + \delta D$, for which we may write

$$r = w_{rA}/-\alpha = w_{rB}/-\beta = w_{rC}/\gamma = w_{rD}/\delta \qquad \text{(IV-12)}$$

To go back to the complex reaction proceeding according to (IV-11), the following equations may be written for the various steps:

$$\left.\begin{aligned} &\alpha_1 A + \beta B \xrightarrow{1} \gamma_1 C \\ &\gamma_1 C \xrightarrow{2} \alpha_1 A + \beta B \\ &\gamma_2 C + \beta_2 B \xrightarrow{3} \delta D \\ &\delta D \xrightarrow{4} \gamma_2 C + \beta_2 B \end{aligned}\right\} \qquad \text{(IV-13)}$$

The kinetics of a reaction is described completely, if the rates of all steps, r_1, r_2, r_3 and r_4, are specified. Then the rate of change of any reactant or product of a complex reaction can be written in terms of the rates of the steps in which this reactant or product is involved, and in terms of the respective stoichiometric coefficients taken with an appropriate sign:

$$\begin{aligned} w_{rA} &= -\alpha_1 r_1 + \alpha_1 r_2 \\ w_{rB} &= -\beta_1 r_1 + \beta_1 r_2 - \beta_2 r_3 + \beta_2 r_4 \\ w_{rC} &= \gamma_1 r_1 - \gamma_1 r_2 - \gamma_2 r_3 + \gamma_2 r_4 \\ w_{rD} &= \delta r_3 - \delta r_4 \end{aligned} \qquad \text{(IV-14)}$$

Obviously, if it were possible to express the rates of change for some reactants or products in terms of rates of change for other reactants or products, the problem of reducing the number of governing equations would be solved, because the concentrations of the former could likewise be expressed in terms of the concentrations of others.

As an example, we shall consider an isothermal reaction proceeding in a batch reactor. We assume that three components are involved in the reaction, with the respective rates of change given by w_{r_1}, w_{r_2} and w_{r_3}. We further assume that the rate of change of the third component may be expressed in terms of those for the remaining two as follows

$$w_{r_3} = aw_{r_1} + bw_{r_2} \tag{IV-15}$$

where a and b are some constants, positive or negative.

Changes in the concentrations of the reaction components with time will then be described by equations of the form:

$$\left.\begin{aligned} \frac{dc_1}{d\tau} &= w_{r_1} \\ \frac{dc_2}{d\tau} &= w_{r_2} \\ \frac{dc_3}{d\tau} &= w_{r_3} \end{aligned}\right\} \tag{IV-16}$$

On the basis of (IV-15), the last line in Eqs. (IV-16) may be re-cast as follows

$$dc_3/d\tau = a\,dc_1/d\tau + b\,dc_2/d\tau$$

Then, on integration, we get

$$c_3 - c_{30} = a(c_1 - c_{10}) + b(c_2 - c_{20})$$

and finally

$$c_3 = c_{30} + a(c_1 - c_{10}) + b(c_2 - c_{20}) \tag{IV-17}$$

which may be used instead of the last line in Eqs. (IV-16).

Since, in one form or another, Eqs. (IV-16) are used in mathematical models for any type of reactor, the above example suggests that the differential equation(s) for one or several components may well be replaced with far simpler linear relationships of the form of (IV-17).

In the above example, it has been assumed that the linear relation, Eq. (IV-15), is known. In practice, this relation has to be evaluated from a system of general equations, Eqs. (IV-14), which gives expressions for the rate of conversion of each component in terms of the rates of the individual reaction steps.

Now we may compile a *matrix* of stoichiometric coefficients for the system of equations, Eqs. (IV-14):

$$\begin{matrix} -\alpha_1 & \alpha_1 & 0 & 0 \\ -\beta_1 & \beta_1 & -\beta_2 & -\beta_2 \\ -\gamma_1 & -\gamma_1 & -\gamma_2 & \gamma_2 \\ 0 & 0 & \delta & -\delta \end{matrix} \tag{IV-18}$$

where the coefficient at the intersection of the ith row and the kth column is the stoichiometric coefficient of the ith component at the kth reaction step, taken with an appropriate sign.

In the general case, the number of rows in the matrix may or may not be equal to the number of columns, that is, the number of reactants in a complex reaction may be equal or unequal to the number of elementary steps.

From matrix theory it is known that if the rows or columns of a matrix are linearly related, the rank of such a matrix is lower than the least of the numbers i and k, where i is the number of rows and k is the number of columns. The *rank of a matrix* is the order of the highest determinant which can be derived from the matrix. Thus the matrices

$$\begin{matrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{matrix} \quad \text{and} \quad \begin{matrix} 1 & 1 & 0 \\ 1 & 1 & -1 \end{matrix}$$

are both of rank 2, because the maximum non-zero determinant that can be constructed for these matrices is of order 2. On the other hand, as can readily be proved, the third-order determinant for the first matrix is zero. In turn, the rank of a matrix defines the number of independent rows, and the determinant constructed to find the rank indicates these rows.

Thus, the selection of limiting reactants reduces to finding the rank of a matrix of stoichiometric coefficients, Eq. (IV-18). The rank of the matrix and, as a consequence, the number of limiting reactants, and the reactants themselves can be determined by known methods of matrix calculus.

With the matrix of (IV-18), the following path can be taken. We shall seek the rank of the matrix by progressively increasing the order of the determinants analysed. The first-order determinant containing only one element is easy to construct—it will suffice to take any non-zero element of the matrix.

The next step is to determine the second-order non-zero determinant. To do so, we take the first determinant in the upper left corner of the matrix, (IV-18):

$$\begin{vmatrix} -\alpha_1 & \alpha_1 \\ -\beta_1 & \beta_1 \end{vmatrix} = -\alpha_1\beta_1 + \alpha_1\beta_1 = 0$$

As is seen, it is equal to zero. It is easy to check that any determinant composed of the rows in the first two columns will likewise be equal to zero, which is an indication of a linear relationship between the first and second columns of the matrix (IV-18). This is so because the second column can be derived from the first by multiplying it by —1.

The same applies to the second-order determinants constructed from the rows of the third and fourth columns, which can likewise be derived from each other by multiplying by —1. Thus, we find that the first and second, and also the third and fourth columns of the matrix are pairwise linearly interrelated. Thus, the matrix cannot be of a higher rank than two.

It remains to analyse the second-order determinants that can be obtained from the rows of the second and third columns. It can be readily seen that for these columns any combination of two rows gives a non-zero determinant, for example

$$\begin{vmatrix} \alpha_1 & 0 \\ \beta_1 & -\beta_2 \end{vmatrix} = -\alpha_1\beta_2 \neq 0 \qquad \begin{vmatrix} \alpha_1 & 0 \\ 0 & \delta \end{vmatrix} = \alpha_1\delta \neq 0, \quad \text{etc.}$$

Thus, we have found that matrix (IV-18) is of rank 2; consequently, two limiting reactants may be chosen. Which reactants will actually be chosen is immaterial because any determinant obtained from the rows of the second and third columns will be non-zero in the general case.

Let the limiting reactants be A and D. Then, as can readily be checked, the rates of conversion for B and C may be expressed in terms of rates of conversions w_{rA} and w_{rD} as follows

$$w_{rB} = \frac{\beta_1}{\alpha_1} w_{rA} - \frac{\beta_2}{\delta} w_{rD}$$

$$w_{rC} = -\frac{\gamma_1}{\alpha_1} w_{rA} - \frac{\gamma_2}{\delta} w_{rD}$$

If A and B are chosen to be the limiting reactants, the following expressions will be obtained for w_{rC} and w_{rD}:

$$w_{rC} = -\frac{\beta_1\gamma_2 + \beta_2\gamma_1}{\alpha_1\beta_2} w_{rA} + \frac{\gamma_2}{\beta_2} w_{rB}$$

$$w_{rD} = \frac{\beta_1\delta}{\alpha_1\beta_2} w_{rA} - \frac{\delta}{\beta_2} w_{rB}$$

Similarly, we may find relationships for any pair of limiting reactants, A and C, B and C, B and D, C and D.

Equilibrium constant for reversible reactions. The term "reversible" applies to reactions that can proceed in both the forward and the reverse directions. In a reversible reaction, the reactants fail to complete conversion in the forward direction (the specific reaction rate is k_1), and the reaction proceeds in the reverse direction (at a specific reaction rate k_2). Under the circumstances, a situation occurs in which the rates of the forward and reverse reactions just balance each other, and a dynamic chemical equilibrium is established, which is defined by the *equilibrium constant*, K_c. Therefore, in calculating reversible chemical reactions, the equilibrium constant should be derived from the law of mass action.

Let a reaction proceed according to the scheme

$$aA + bB \underset{k_2}{\overset{k_1}{\rightleftharpoons}} rR + sS$$

where A and B are the reactants, R and S are the products of the reaction, a, b, r and s are the respective stoichiometric coefficients.

Then, according to the law of mass action

$$K_c = \frac{c_R^r c_S^s}{c_A^a c_B^b} = k_1/k_2 \qquad \text{(IV-19)}$$

where K_c is the equilibrium constant (at t = constant) characteristic of a given reversible reaction; c_A, c_B, c_R and c_S are the concentrations of the reactants and products at equilibrium, in moles per litre; k_1 and k_2 are the rate constants for the forward and reverse reactions, in s^{-1}.

It is customary to write a reaction in the direction accompanied by the liberation of heat. Then the concentrations of the reacting species on the right-hand side are written in the numerator and those on the left-hand side in the denominator of Eq. (IV-19).

For gas-phase reactions, concentrations are usually replaced with the partial pressures of the reacting species. In such cases, the equilibrium constant takes the form

$$K_p = \frac{p_R^r p_S^s}{p_A^a p_B^b} \tag{IV-20}$$

where p_A, p_B, p_R and p_S are the partial pressures of the reacting species.

The partial pressure of a gas may be defined as

$$p = NRT/V = cRT \tag{IV-21}$$

whence

$$K_p = \frac{(c_R RT)^r (c_S RT)^s}{(c_A RT)^a (c_B RT)^b} \tag{IV-22}$$

Solving Eqs. (IV-21) and (IV-22) simultaneously gives the following connection between K_p and K_c

$$K_p = K_c (RT) \exp [(r+s)-(a+b)] \tag{IV-23}$$

It follows from the above relationship that at $(a+b) = (r+s)$ a reaction will proceed at constant volume and the numerical value of the equilibrium constant will be independent of the units in which the concentrations are expressed. In other words, for reactions proceeding at constant volume the state of equilibrium is independent of the pressures of inert impurities. The equilibrium concentrations of the reacting species will however be pressure-dependent.

Let there be a heterogeneous reaction in which A and R are gases, and B and S are solids. Then the concentrations of B and S in the gas phase will be constant and, as a consequence, Eq. (IV-23) will take the form

$$K_c \frac{c_B^b}{c_S^s} = K_c' = \frac{c_R^r}{c_A^a} \tag{IV-24}$$

Thus, the concentrations of the reacting species present in a condensed (solid or liquid) phase are lumped with the constant K_c'.

The effect of temperature on the equilibrium constant is described by the van't Hoff thermodynamic equation

$$d(\ln K_c)/dT = H_v/RT^2 \tag{IV-25}$$

or

where H_v and H_p are the heat effects of a reaction at constant volume and constant pressure, respectively, in kJ/kmole and R is the universal gas constant equal to 8.314 kJ kmole^{-1} deg^{-1}.

On integrating between the limits of temperature, T_2 and T_1, Eqs. (IV-25) and (IV-26) take the form

$$\ln (K_{c1}/K_{c2}) = \frac{(H_v)_{av}}{R} \frac{T_2-T_1}{T_2T_1} \tag{IV-27}$$

or

$$\ln (K_{p1}/K_{p2}) = \frac{(H_p)_{av}}{R} \frac{T_2-T_1}{T_2T_1} \tag{IV-28}$$

where $(H_v)_{av}$ and $(H_p)_{av}$ are the average heat effects of a reaction at constant volume and constant pressure, respectively, over a given temperature range.

With a rise in equilibrium temperature the fractional conversion increases for endothermic reactions and decreases for exothermic reactions. In gas-phase variable-volume reactions the fractional conversion increases if the number of moles decreases with the progress of the reaction and decreases if the number of moles increases. Once the equilibrium constant is known, it is an easy matter to determine the equilibrium amounts of the reacting species for a given reaction and, hence, the maximum yields of reaction products under specified conditions.

In practice, as a way of enhancing the throughput of a reactor, optimum operating conditions, notably residence times for the reactants, are found separately in each particular case. Ordinarily, the conversion is assumed to be 85 to 90% of its equilibrium value. It should be remembered, however, that the above reasoning applies to cases where $K_c < 1$. At $K_c \gg 1$, reactions will be irreversible.

IV-2. MATHEMATICAL MODELS OF ISOTHERMAL REACTORS

(A) THE PLUG-FLOW MODEL (TUBULAR REACTORS)

On the basis of Eq. (II-31) and with a chemical reaction taking place, a plug-flow reactor may be described by an equation of the form

$$\partial c_1/\partial \tau = -w(\partial c/\partial x) + w_r \tag{IV-29}$$

For a reaction of an arbitrary nth order, the rate equation may be written as

$$(-w_r) = kc_A^n \tag{IV-30}$$

Defining the fractional conversion as

$$x_A = (c_{A0}-c_A)/c_{A0}$$

where c_{A0} and c_A are the initial and final concentrations of the reactant, we get

$$dx/d\tau = kc_{A0}^{n-1}(1-x_A)^n \tag{IV-31}$$

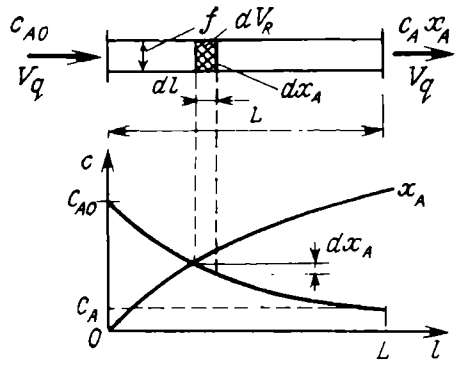


Fig. IV-1. Plug-flow reactor model

To take care of changes in the concentration of reactant A with reactor length, l (Fig. IV-1), under steady-state conditions, we shall re-write Eq. (IV-29) as follows:

$$-w\frac{dc_A}{dl}+(-w_r)=0$$

or

$$w(dc_A/dl)=(-w_r) \qquad \text{(IV-32)}$$

If the reactor tube has a constant cross-section, f, then an element of volume within the element of length dl will be

$$dV_R = fdl$$

Recalling that with a plug flow the space or volumetric velocity is constant, that is, $V_q = fw$ = constant, we may re-write Eq. (IV-32) as

$$V_q(dc_A/dV_R)=(-w_r) \qquad \text{(IV-33)}$$

Noting Eqs. (IV-30) and (IV-31), separating the variables and integrating, we find

$$V_R/V_q = -\int_{c_{A0}}^{c_A} dc_A/w_r = -\int_{c_{A0}}^{c_A} dc_A/kc_A^n = -c_{A0}\int_0^{x_A} dx/w_r$$

$$=\frac{1}{k}c_{A0}^{1-n}\int_0^{x_A} dx/(1-x_A)^n = \tau \quad \text{seconds} \qquad \text{(IV-34)}$$

Hence, for $n \neq 1$,

$$\tau = \frac{c_{A0}^{1-n}}{(n-1)k}[(1-x_A)^{1-n}-1] \quad \text{seconds} \qquad \text{(IV-35)}$$

At $n = 1$,

$$\tau = \frac{\ln(1-x_A)}{k} \quad \text{seconds} \qquad \text{(IV-36)}$$

where τ is the residence time for a plug-flow reactor.

If the time needed for a reaction to reach completion is the same as the residence time (as should be from the definition of a plug-flow reactor), then the above equation describing a plug-flow reactor checks fully with the integral equation of classical reaction kinetics.

The plug-flow model is applicable to continuous-flow tubular reactors at $L/d_T > 100$, where d is the tube diameter under conditions of turbulent flow, since a well-pronounced turbulence effectively equalizes the velocity and concentration profiles.

(B) BATCH REACTORS

A batch reactor accommodates a charge of reactants and causes them to react at an acceptable rate to give the desired product. Most batch reactors are equipped with an agitator to stir the reaction mixture and with some means of heating or cooling. At the end of the specific time interval, the products are discharged, and the reactor is brought to readiness to accept the next batch of feed stock. At each particular instant, the concentrations of the reacting components are the same throughout the volume of the stock, but are continually changing with time until the desired final concentration or the desired fractional conversion is attained.

In other words, in a batch reactor the concentration of the stock at a particular instant is different from that existing at the previous instant. In this sense a batch reactor may be looked upon as a reactor with a plug flow occurring in time. This is, of course, an idealization because a perfect homogeneity of stock concentration is assumed in any cross-section of the reactor volume.

Consider a batch reactor of effective volume (reactor holdup) V_R charged with a reaction mixture containing initially N_A moles of reactant A. Since the process proceeds in time, from a material balance on the reactant A we have

$$-dN_A = w_r V_R \, d\tau \tag{IV-37}$$

Since

$$dN_A = d(c_A V_R) \tag{IV-38}$$

Eq. (IV-37) may be re-written as follows:

$$-d(c_A V_R)/V_R \, d\tau = w_r \tag{IV-39}$$

Hence,

$$-dc_A/d\tau = w_r \tag{IV-40}$$

In view of Eqs. (IV-30) and (IV-31), we get

$$-dc_A/d\tau = kc_A^n \tag{IV-41}$$

$$dx_A/d\tau = kc_{A0}^{n-1}(1-x_A)^n \tag{IV-42}$$

The residence time is then

$$\tau = -\int_{c_{A0}}^{c_A} dc_A/kc_A^n = \frac{1}{k} c_{A0}^{1-n} \int_0^{x_A} dx_A/(1-x_A)^n \quad \text{seconds} \tag{IV-43}$$

Thus, the equation describing a batch reactor is fully identical with Eq. (IV-34) applicable to the plug-flow reactor. It is important to remember, however, that a batch reactor is only analogous to a plug-flow reactor in which the plug flow takes place over time rather than over length.

(C) THE COMPLETE MIXING MODEL (CONTINUOUS STIRRED TANK REACTORS)

On the basis of Eq. (II-32) and with a chemical reaction taking place, the complete-mixing model can be described by a kinetic equation of the form

$$(-w_r) = V_q/V_R(c_{in}-c) = (V_q/V_R)(c_{A0}-c_A) \tag{IV-44}$$

Hence, the residence time for reactant A is

$$\tau = V_R/V_q = (c_{A0}-c_A)/(-w_r) = (c_{A0}-c_A)/kc_A^n$$
$$= c_{A0}^{1-n}x_A/[k(1-x_A)^n] \quad \text{seconds} \tag{IV-45}$$

For first-order reactions, Eq. (IV-45) takes the form

$$k\tau = x_A/(1-x_A) \tag{IV-46}$$

This relationship can alternately be derived from the transfer function of a simple-lag element (see p. 24):

$$c_{A,\,out}(0)/c_{A,\,in}(0) = 1/(kT+1)$$

Substituting in the above equation the fractional conversion

$$x_A = (c_{A,\,in}-c_{A,\,out})/c_{A,\,in}$$

and noting that the time constant $T = \tau = V_R/V_q$, we get Eq. (IV-46)

$$kT = k\tau = x_A/(1-x_A)$$

From the above equation and Eq. (IV-46) it follows that the quantity $k\tau$ may serve as a measure of *process efficiency*.

(D) THE DISPERSION MODEL (CONTINUOUS STIRRED TUBULAR REACTORS)

According to Eq. (II-35), for a continuous flow tubular reactor we get

$$\frac{dc}{d\tau} = -w\frac{dc}{dx} + D_L\frac{d^2c}{dx^2} + \frac{D_R}{R}\frac{\partial}{\partial R}\left(R\frac{\partial c}{\partial R}\right) + (-w_r) \tag{IV-47}$$

With only longitudinal mixing and under steady-state conditions, the following dimensionless expression is obtained

$$-(dc/dz) + (D_L/wL)(d^2c/dz^2) - k\tau c_A^n = 0 \tag{IV-48}$$

or, introducing the fractional conversion for reactant A,

$$-(dx_A/dz) + (D_L/wL)(d^2x_A/dz^2) + k\tau c_A^{n-1}(1-x_A)^n = 0 \tag{IV-49}$$

For first-order reactions, the solution of Eq. (IV-49) is

$$\frac{c_A}{c_{A0}} = 1-x_A = \frac{4a\exp\left(\frac{1}{2}\frac{wL}{D_L}\right)}{(1+a)^2\exp\left(\frac{a}{2}\frac{wL}{D_L}\right) - (1-a)^2\exp\left(-\frac{a}{2}\frac{wL}{D_L}\right)} \tag{IV-50}$$

where

$$a = \sqrt{1+4k\tau(D_L/wL)}$$

For small deviations from an ideal plug flow, that is, for small values of D_L/wL, the following relationships are obtained between the real reactor (V_R, L_R, τ_R) and an ideal plug-flow model (V_{Rb}, L_{Rb}, τ_{Rb}):

for the same fractional conversion

$$L_R/L_{Rb} = V_R/V_{Rb} = \tau_R/\tau_{Rb} = 1+k\tau(D_L/wL) = 1+kD_L/w^2 \quad \text{(IV-51)}$$

for the same size

$$c_{AR}/c_{Ab} = 1+(k\tau)^2 D_L/wL \quad \text{(IV-52)}$$

The ratio of the real reactor volume to that of the ideal plug-flow reactor, V_R/V_{Rb}, as a function of the reaction of the reactant remaining unreacted for a set of values of D_L/wL and for first- and second-order reactions is

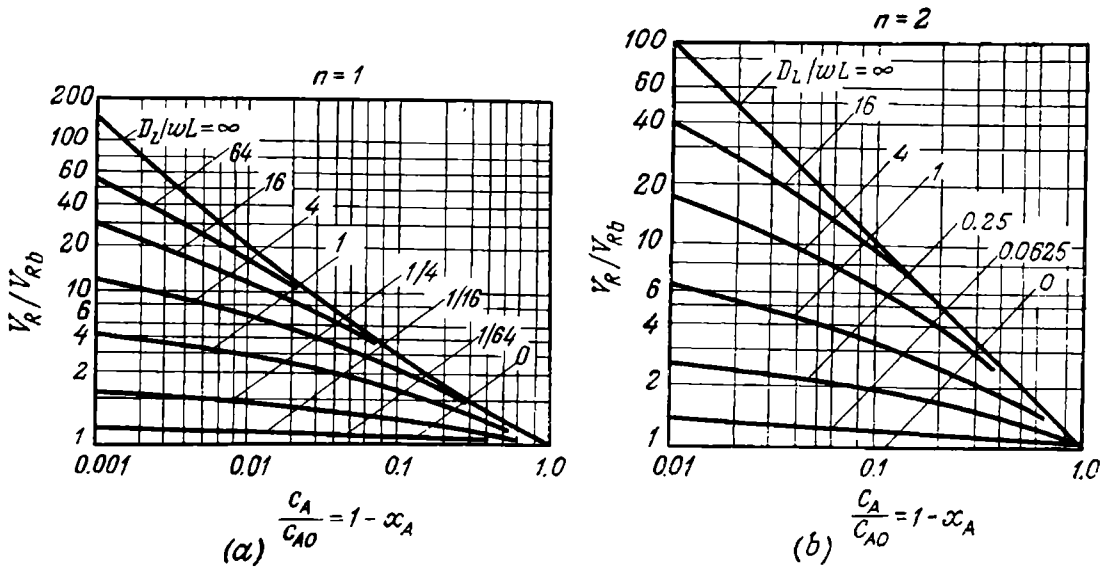


Fig. IV-2. Real to ideal reactor volume ratio as a function of the fraction of reactant remaining unreacted

(*a*) first-order reaction; (*b*) second-order reaction

plotted in Fig. IV-2. The value of D_L/wL for fractional-order reactions can be obtained by interpolating the plotted data. The value of D_L/wL found from the plot of Fig. IV-2 should then be multiplied by the dimensionless ratio d_T/L.

(E) THE STIRRED TANK CASCADE MODEL

In practice, well-stirred tanks are often arranged in a cascade (Fig. IV-3) in order to carry to completion a reaction that cannot be brought to a final state in a single tank or in order to secure a more intimate mixing of the reacting species.

Referring to Fig. IV-3, each tank in a cascade may be visualized as a step change in the concentration of a reactant. On drawing a quiet curve through the corners of the steps, we obtain a curve similar to that of a plug-flow reactor. Obviously, with a progressive increase in the number of single stirred tank reactors in a cascade we shall as progressively be approaching a plug-flow reactor. Conversely, a plug-flow tubular reactor may be looked upon as a cascade of a very great number of continuous stirred tank reactors having the same overall hold-up volume.

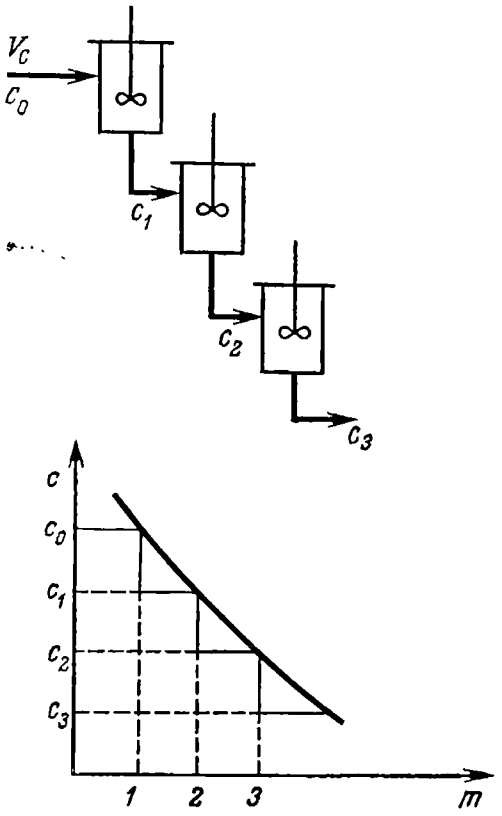


Fig. IV-3. Cascade model
c — concentration; m — number of stages

Design equations for a cascade of continuous stirred tank reactors can be derived in several ways. Some of them are discussed below.

The algebraic method. From the foregoing, the residence time for a single stirred tank reactor is

$$\tau = \frac{c_{A0} - c_A}{(-w_r)}$$

Let the concentration of the reactant leaving the last tank be c_{Am}, where m is the number of cascaded reactors. Then for a cascade of equal-size tanks we shall have

$$\tau_m = \frac{c_{m-1} - c_{Am}}{(-w_r)}$$

or

$$c_{Am} - \tau_m w_r = c_{Am-1}$$

For first-order reactions,

$$(-w_r) = kc_{Am}$$

and so

$$c_{Am} + \tau_m k c_{Am} = c_{Am}(1 + k\tau_m) = c_{Am-1}$$

whence

$$c_{Am} = c_{Am-1}/(1 + k\tau_m)$$

$$c_{A1} = c_{A0}/(1 + k\tau_1)$$

$$c_{A2} = c_{A1}/(1 + k\tau_2) = c_{A0}/(1 + k\tau_1)(1 + k\tau_2)$$

If the residence time is the same for each of the reactors, then

$$c_{Am} = c_{A0}/(1 + k\tau)^m \qquad \text{(IV-53)}$$

Taking a logarithm of the last equation, we obtain the number of reactors in the cascade

$$m = \log_{10}(c_{A0}/c_{Am})/\log_{10}(1+k\tau) \qquad \text{(IV-54)}$$

For high-order reactions, it is increasingly more difficult to express c_{Am} in terms of c_{A0}, and the algebraic method loses its value.

For a cascade of m reactors with an overall hold-up V, the residence time for the system is $\tau = V/V_q$, and the average residence time per tank is τ/m. Under the circumstances, the fractional conversion for a cascade of reactors may be defined by

$$x_A = 1 - \frac{1}{(1+k\tau/m)^m} \qquad \text{(IV-55)}$$

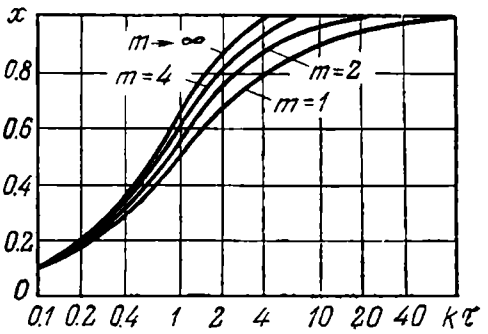


Fig. IV-4. Fractional conversion for different number of reactors in a cascade

In graphical form, the above equation is shown in the plot of Fig. IV-4. Since the product $k\tau$ is directly proportional to volume, it follows from the plot that for all values of x_A the volume $1/k\tau$ (that is, per reactor) will decrease with increasing number of reactors and increasing fractional conversion. These relations are presented in Table IV-1.

The number of reactors in a cascade and the overall hold-up of the system may conveniently be found from the plot of Fig. IV-4 and Table IV-1 as follows. Assuming that the inlet and outlet concentrations in the system are the same for different numbers of reactors, we find the values of $k\tau$ at $x = 0.9$. Then

$$m = 1 \quad k\tau_1 = 9$$
$$m = 2 \quad k\tau_2 = 4.3 = 0.48\, k\tau_1$$
$$m = 3 \quad k\tau_3 = 3.1 = 0.34\, k\tau_1$$

It is seen that the total hold-up volume of a cascade may be nearly halved with two reactors and reduced by a third with three reactors as compared with a single tank reactor.

Table IV-1

Relative Volume of m Reactors in a Cascade

m	$x = 0.5$		$x = 0.9$		$x = 0.98$	
	$k\tau$	$1/k\tau$	$k\tau$	$1/k\tau$	$k\tau$	$1/k\tau$
1	1	1	9	1	50	1
2	0.82	1 : 1.2	4.3	1 : 2.1	12.2	1 : 4.1
3	0.76	1 : 1.3	3.1	1 : 2.9	6.6	1 : 7.6

Numerical iteration. Using the iterative scheme, we can readily derive the design equation and its solution for any order of reaction, n, for any number m of reactors in a cascade, and for any reactor hold-up.[3]

As before, for an nth-order reaction the design equation of a single stirred tank reactor may be written as

$$c_0 - c_m = k(V_R/V_q)c_m^n \tag{IV-56}$$

On re-writing,

$$1 - c_m/c_0 = (2k/2)(V_R/V_q)\, c_0^{n-1}(c_m/c_0)^n \tag{IV-57}$$

On putting

$$R = 2k(V_R/V_q)c_0^{n-1} \tag{IV-58}$$

$$\nu = c_m/c_0 \tag{IV-59}$$

we get

$$f(\nu) = (R/2)\nu^n + \nu - 1 = 0 \tag{IV-60}$$

The fractional conversion is found as a root of Eq. (IV-60) located between 0 and 1.

The solution can be obtained by iteration, using Newton's method to speed up convergence. Since

$$f'(\nu) = (nR/2)\nu^{n-1} + 1$$

Newton's iteration formula takes the form

$$\nu_{\alpha+1} = \nu_\alpha - \frac{(R/2)\nu_\alpha^n + \nu_\alpha - 1}{(nR/2)\nu_\alpha^{n-1} + 1} \tag{IV-61}$$

where α is the iteration cycle number and n is the reaction order.

With Eq. (IV-61), one can solve Eq. (IV-60) for any order of reaction. For the first cycle of iteration we may take $\nu_\alpha = 1$.

Equations (IV-58) through (IV-60) may be written for any ith reactor in a cascade as follows

$$R_i = 2k_i(V_{Ri}/V_q)c_{i-1}^{n-1} \tag{IV-58a}$$

$$\nu_i = c_i/c_{i-1} \tag{IV-59a}$$

$$(R_i/2)\nu_i^n + \nu_i - 1 = 0 \tag{IV-60a}$$

where $i = 1, 2, \ldots, m-1, m$.

Equation (IV-60a) may be solved for any reactor of any hold-up, starting with the first one.

The final concentration of reactants, or the fraction of the material remaining unreacted in the exit stream, $\nu = c_m/c_0$, will be

$$\nu = \nu_1\nu_2\nu_3 \ldots \nu_{m-1}\nu_m \tag{IV-62}$$

Example IV-1. A reaction whose kinetics is described by the equation

$$w_r = 1.6c_c^{0.76} \text{ moles litre}^{-1} \text{ min}^{-1}$$

takes place in a continuous stirred tank reactor with a hold-up of $V_R = 200$ litres.

Find the fractional conversion, if the feed stock is admitted at a rate of $V_q = 400$ litres/min and the starting concentration is $c_0 = 1.2$ kmoles/litre.

Solution. The value of R is given by Eq. (IV-58) to be:

$$R = 2k(V_R/V_q)c_0^{n-1} = 2(1.6)\,(200/400)\,1.2^{0.76-1} = 1.53$$

For $n = 0.76$, Eq. (IV-61) gives ν to be:

$$\nu = 1 - \frac{(1.53/2)\times 1^{0.76}+1-1}{\left(\frac{0.76\times 1.53}{2}\right)\times 1^{0.76-1}+1} = 0.53$$

Hence, the fractional conversion is

$$100(1-\nu) = 100(1-0.53) = 47\%$$

Example IV-2. Solve the problem of Example IV-1, assuming that the reaction is carried out in two reactors in series.

Solution. For the first reactor:

$$R_1 = 1.53$$

$$\nu_1 = 0.53$$

Then for second reactor:

$$R_2 = 2(1.6)\,(200/400)\,(1.2\times 0.53)^{0.76-1} = 1.783$$

By Eq. (IV-61), we obtain

$$\nu_2 = 1 - \frac{(1.783/2)\times 1^{0.76}+1-1}{\frac{(0.76\times 1.783)}{2}\times 1^{0.76-1}+1} = 0.485$$

By Eq. (IV-62), we find

$$\nu = \nu_1\nu_2 = 0.53\times 0.485 = 0.257$$

Hence, the fractional conversion is

$$100(1-0.257) = 74.3\%$$

Because of the relatively small curvature of the $f(\nu)$ curve one cycle of iteration proves sufficient in the above problems.

The graphic method. The equation describing a well-stirred reactor may be reduced to the form

$$w_r = -c_m/\tau_m + c_{m-1}/\tau_m \qquad \text{(IV-63)}$$

At a given inlet concentration, c_{m-1}, Eq. (IV-63) is linear in exit concentration.

A plot of the right-hand side of Eq. (IV-63) in the w_r-*vs*-c coordinates yields a straight line whose slope is $1-1/\tau_m$ and which intersects the axis of abscissae at the point representing the inlet concentration (Fig. IV-5). The abscissa of the point where this straight line intersects the curve described

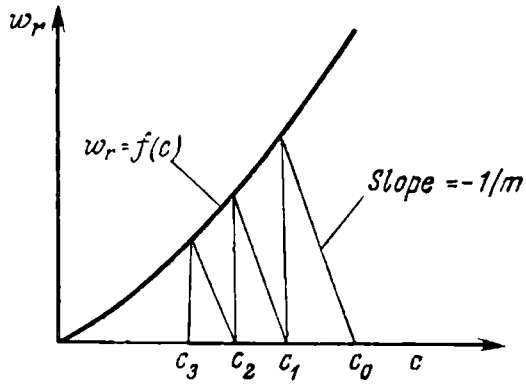


Fig. IV-5. Graphical representation of the number of reactors in a cascade

by the rate equation, $w_r = f(c)$, gives the exit concentration for each stage in a cascade and at the inlet to the next one. With equal-sized reactors in a cascade, the residence time is the same throughout the system, and the straight lines are parallel. The construction is carried on until the desired concentration is attained (see Fig. IV-5). The number of points thus obtained gives the number m of reactors (in the Figure, $m = 3$).

IV-3. REACTOR DESIGN FROM RESPONSE CURVES, NEGLECTING SYSTEM MACROSTATE. REACTOR EFFECTIVENESS FACTOR

System response curves. Going back to the mathematical model of a unit in which a linear process takes place (for example, a first-order chemical reaction or a diffusion process), the model can be derived on the basis of additivity as follows

[data on unit residence time] − [data on kinetics of the process with a rate linear in concentration] → [mathematical model of the linear system]

In other words, if we have an experimental response curve or residence time distribution, $C(\tau)$, for a given type of unit and data on the process kinetics as the value of $c_A = f(\tau)$, we can determine the fractional conversion for a real reactor.

Let V_q designate the space or volumetric velocity of the feed stream admitted to the system, V_t the total amount of a tracer material injected into the system, and c_t the instantaneous concentration of the tracer. Let also the tracer be carried by the stream in time $\Delta\tau$ through a limited area ΔF where a chemical reaction takes place and where the true velocity of the stream lies in the range from w to $(w+\Delta w)$, such that Δw is negligible in comparison with w.

From a material balance we get

$$c_t V_q \Delta\tau = c_{t0} w \Delta F \qquad \text{(IV-64)}$$

where c_{t0} is the concentration of the tracer material in the impulse, $\Delta\tau$ is the duration of the impulse, f is the fraction of ΔF for the liquid stream.

Since the total amount of tracer material injected is

$$V_t = V_q c_{t0} \Delta\tau$$

then

$$V_q^2 c_t \Delta\tau = V_t w f \Delta F \qquad \text{(IV-65)}$$

or

$$f\Delta F = \frac{V_q^2 c_t \Delta\tau}{V_t w} \tag{IV-66}$$

For a first-order reaction we have

$$-dc/d\tau = kc$$

$$c_f/c_s = \exp(-k\tau) \tag{IV-67}$$

where τ is the time that the stream passes through the reactor, c_s is the initial concentration and c_f is the final concentration.

Let c_{out} be the total amount of tracer material leaving the reactor per unit time, c_{in} the total amount of reactant entering the reactor per unit time, and Δc_{out} the amount of reactant in the liquid stream passing through the reactor cross-section ΔF per unit time. Then

$$\Delta c_{out} = c_f w f \Delta F \tag{IV-68}$$

Substituting for $f\Delta F$ its expression from Eq. (IV-66), we get

$$\Delta c_{out} = \frac{c_f V_q^2 c_t w \Delta\tau}{V_t w} = \frac{c_f V_q^2 c_t \Delta\tau}{V_t}$$

Substituting for c_f its expression from Eq. (IV-67), we obtain

$$\Delta c_{out} = \frac{c_s V_q^2 c_t e^{-k\tau} \Delta\tau}{V_t} \tag{IV-69}$$

For the entire reactor,

$$c_{out} = \sum_1^\infty \Delta c_{out} = \frac{c_s V_q^2}{V_t} \sum_{i=1}^\infty c_t e^{-k\tau} \Delta\tau \tag{IV-70}$$

where the summation is carried out over all $\Delta\tau_i$.

The amount of reactant entering the reactor per unit time is $V_q c_s = c_{in}$. Then the fraction of the reactant remaining unreacted will be

$$c_{out}/c_{in} = (V_q/V_t) \sum_1^\infty c_t e^{-k\tau} \Delta\tau_i \tag{IV-71}$$

As $\Delta\tau \to 0$, in the limit we obtain an integral expression

$$c_{out}/c_{in} = V_q/V_t \int_0^\infty c_t e^{-k\tau} d\tau \tag{IV-72}$$

Using Eq. (IV-63) and the system response curve for any level of conversion, we can find the reaction rate constant. The total amount of tracer injected, V_t, can be found from the system response curve as the area under that curve. Noting the response curve, Eq. (IV-72) may be reduced to the form

$$c_f/c_s = \int_0^\infty C(\tau) e^{-k\tau} d\tau \tag{IV-73}$$

In practice, the reaction kinetics can hardly be divorced from the factors contributed by the flow pattern. As a way out, the value of $C(\tau)$ is obtained as usual, from the system response curve, after which the reaction rate constant k is found by trial and error to obtain the desired fractional conversion or to satisfy the ratio c_f/c_s. This value of k will be the true rate constant for a reaction taking place under actual conditions, because it will solely depend on the chemical and kinetic factors affecting the process and be fully independent of the amount of mixing or the conduct of the process.

Reactor effectiveness factor. The reactor effectiveness factor whose meaning will become clear from the subsequent discussion can be determined as follows.

Let there be a first-order reaction for which we assume an arbitrary, but sufficiently high fractional conversion of 90% ($c_f/c_s = 0.1$). Ordinarily, this is sufficient for any change in residence time to be noticed from the distribution diagram (the system response curve).

Using the response curve of the reactor and Eq. (IV-73), we find the pseudo-rate constant, k, of the hypothetical reaction at which the desired fractional conversion (90%) is attained:

$$c_f/c_s = 0.1 = \int_0^\infty C(\tau)e^{-k\tau}\,d\tau$$

The residence time, τ, can be found from Eq. (II-2):

$$\tau = \tau_{av} = \frac{\int_0^\infty \tau c_t\,d\tau}{\int_0^\infty c_t\,d\tau} \approx \frac{\sum \tau c}{\sum c} \text{ seconds}$$

Taking an ideal plug-flow reactor as a reference (100% conversion), we next find the residence time needed to attain a conversion of 90% in a real plug-flow reactor at the pseudo-rate constant, k.

For first-order reactions in a plug-flow reactor we get:

$$c_f/c_s = 0.1 = e^{-k\tau_b}$$

or

$$\tau_b = -\ln (c_f/c_s)/k$$

where τ_b is the residence time in the ideal plug-flow reactor. Then, the effectiveness factor of the reactor will be

$$\eta = (\tau_b/\tau_{av}) \times 100\% \qquad \text{(IV-74)}$$

The effectiveness factor for several reactors is plotted in Fig. IV-6.[4] As is seen, it comes closely to 100% for several reactors where the fractional

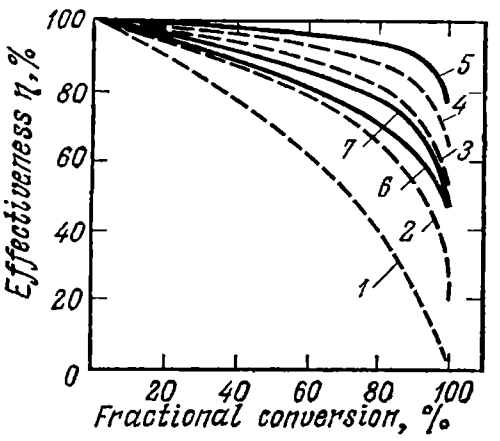


Fig. IV-6. Efficiency of several reactors

1 — stirred reactor; *2* — two stirred reactors in series; *3* — three stirred reactors in series; *4* — four stirred reactors in series; *5* — reactor with a stagnant region (pilot plant); response curve is shown in Fig. IV-7*a*; *6* — commercial reactor with a stagnant region; response curve is shown in Fig. IV-7*b*; *7* — commercial reactor with a stagnant region; response curve is shown in Fig. IV-7*c*

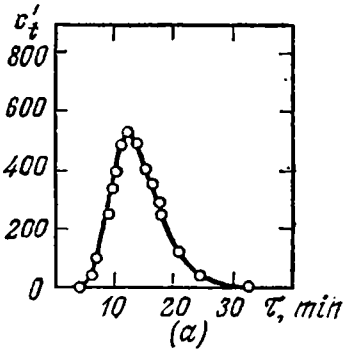
conversion is low. As the conversion increases, the effectiveness factor decreases, and the difference among the various reactors becomes more pronounced. It may be added that reactors having the same effectiveness factor show identical response curves.

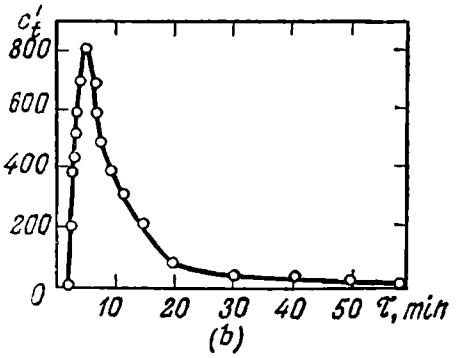
The response curves of a pilot and a commercial reactor are presented in Fig. IV-7. Referring to Fig. IV-7*a*, the response curve of the pilot reactor closely approaches that of an ideal plug-flow reactor but differs markedly from that of the commercial reactor (Fig. IV-7*b* and *c*). After the catalyst is changed to eliminate channelling, the effectiveness factor and the residence time distribution of the commercial reactor improve considerably (Fig. IV-7*c*).

Example IV-3. The reactor of Example II-1 is used for a liquid-phase decomposition reaction whose rate equation is

$$-w_{rA} = kc_A$$

where the rate constant is $k = 0.307$ min^{-1}.





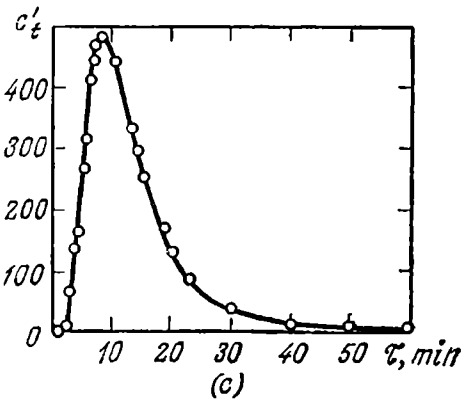


Fig. IV-7. Response curves of pilot and commercial reactors

(*a*) pilot reactor ($\tau_{av} = 14.5$ min, $\eta = 89.5\%$); (*b*) commercial reactor ($\tau_{av} = 10.5$ min, $\eta = 63.5\%$); (*c*) commercial reactor after catalyst change-round ($\tau_{av} = 13.9$ min, $\eta = 70\%$); c'_t — relative concentration of tracer material

Determine the fraction of the reactant remaining unreacted in the real reactor and compare it with that of an ideal plug-flow unit comparable in size. The average residence time is $\tau_{av} = 15$ min.

Solution. For a constant-volume ideal plug-flow reactor we may write

$$\tau = \int_0^{x_A} dx_A/-w_{rA} = -\frac{1}{k}\int_{c_{A0}}^{c_A} dc_A/c_A = \frac{1}{k}\ln(c_{A0}/c_A)$$

where

$$c_A/c_{A0} = e^{-k\tau} = e^{-(0.307\times 1.5)} = 0.01$$

Thus, the fraction of the reactant remaining unreacted in an ideal plug-flow reactor is 1%. For a real reactor, the fraction of the reactant remaining unreacted can be found by Eq. (IV-73). For convenience, all data are summarized in Table IV-2. As is seen, the fraction of the reactant remaining unreacted for the real unit is 4.7%.

Table IV-2

τ	$C(\tau)$	$k\tau$	$e^{-k\tau}$	$e^{-k\tau}C(\tau)\,\Delta\tau$
5	0.03	1.53	0.2154	$0.215\times 0.03 = 0.0323$
10	0.05	3.07	0.0474	0.0116
15	0.05	4.60	0.0100	0.0025
20	0.04	6.14	0.0021	0.0004
25	0.02	7.68	0.0005	0.0001
30	0.01	9.21	0.0001	0
				$\sum e^{-k\tau}C(\tau)\,\Delta\tau = 0.0469$

IV-4. EFFECTIVENESS OF VARIOUS REACTORS

For the purpose of comparison in terms of effectiveness, it is usual to select two extremes of reactor models, namely the plug-flow model and the complete mixing model. We shall carry out the comparison on a simple first-order reaction.

According to Eq. (IV-36), for the plug-flow model we may write

$$\tau_b = -\ln(1-x_A)/k$$

According to Eq. (IV-46), for the complete mixing model we may write

$$\tau_m = x_A/k(1-x_A)$$

Dividing the second equation into the first gives:

$$\tau_m/\tau_b = -x_A/(1-x_A)\ln(1-x_A) \qquad \text{(IV-75)}$$

In graphical form, Eq. (IV-75) is shown in Fig. IV-8. As is seen, the residence time needed for the well-stirred reactor doubles at $x = 70\%$ and trebles at $x = 85\%$. Since the residence time is directly proportional to the reactor hold-up, we find that a well-stirred reactor will always need to have a larger hold-up than a plug-flow reactor. With the same size, a plug-flow reactor will always give a higher conversion than a well-stirred reactor. The hold-up ratio increases with increasing reaction order; it is only with zero-order reactions that the hold-up is the same for both types of reactor.

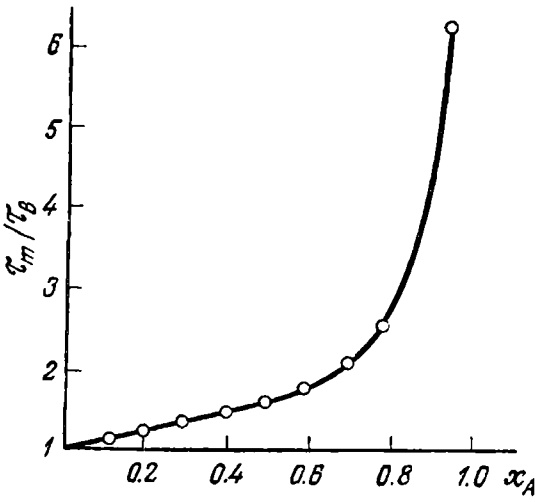


Fig. IV-8. Relative residence time as a function of fractional conversion

If the system volume increases in the course of a reaction, the hold-up ratio also increases, and vice versa.

As the reaction mixture progresses through a plug-flow reactor, the value of x increases with reactor length. Since for simple reactions an increase in x entails a reduction in the reaction rate, the average rate will lie anywhere between its maximum value at the reactor inlet and its minimum value at the exit.

As the reaction mixture advances through a well-stirred reactor, the value of x at any point in the reactor is the same as it is at the reactor exit, and the average rate of the process is the same as the flow rate at the reactor exit.

Under isothermal conditions and at the same fractional conversion at the exit, a plug-flow reactor will always show a higher average reaction rate; as a consequence, the needed hold-up volume will always be smaller than with a well-stirred reactor.

The final concentrations of the reacting species for plug-flow and well-stirred reactors and the respective residence times under isothermal conditions are summarized in Table IV-3. From this table, it is an easy matter to find the yield, selectivity and fractional conversion for various reactions.

Apart from the fractional conversion, the effectiveness of a reactor affects also the breakdown of reaction products. As an example, we shall consider the decomposition of reactant A which can take two paths:

$$a_1A \xrightarrow{k_1} R \quad \text{(wanted product)}$$

$$a_2A \xrightarrow{k_2} S \quad \text{(unwanted product)}$$

according to the kinetic equations:

$$w_{rR} = dc_R/d\tau = k_1c_A^{a_1} \tag{IV-76}$$

$$w_{rS} = dc_S/d\tau = k_2c_A^{a_2} \tag{IV-77}$$

Table IV-3

Final Concentrations and Residence Times of Reacting Components in Plug-Flow and Well-Stirred Reactors under Isothermal Conditions

Reaction	Order	Basic differential equations	Plug-flow reactor	Well-stirred reactor
Irreversible	1	$-\frac{dc_A}{d\tau} = kc_A$	$c_A = c_{A0}e^{-k\tau}$	$c_A = \frac{c_{A0}}{k\tau+1}$
	2	$-\frac{dc_A}{d\tau} = kc_A^2$	$\frac{1}{c_A} = \frac{1}{c_{A0}} + k\tau$	$c_A = a^2 + 2ac_{A0}^{1/2};\quad a = \frac{2k}{\tau}$
$A \rightarrow R$	$^1/_2$	$-\frac{dc_A}{d\tau} = kc_A^{1/2}$	$c_A = [c_{A0}^{1/2} - 0.5k\tau]^2$	$c_A = c_{A0} + 0.5a^2 - a\left(c_{A0} - \frac{a^2}{4}\right)^{1/2};$ $a = k\tau$
	n	$-\frac{dc}{d\tau} = kc_A^n$	$c_A^{1-n} - c_{A0}^{1-n} = (n-1)k\tau$	$\tau = \frac{c_{A0}-c_A}{kc_A^n}$
$A+B \rightarrow R$ $A+B \rightarrow R+S$	2	$-\frac{dc_A}{d\tau} = kc_Ac_B$	$M \neq 1$	$M \neq 1 M = \frac{c_{B0}}{c_{A0}}$
		$\frac{dx_A}{d\tau} = k(1-x_A)(M-x_A)$	$\frac{1}{1-M}\ln\left[\frac{M(1-x_A)}{M-x_A}\right] = c_{A0}k\tau$	$\frac{x_A}{(1-x_A)(M-x_A)} = c_{A0}k\tau$
			$M = 1$	$M = 1$
			$\frac{x_A}{1-x_A} = c_{A0}^2k\tau$	$\frac{x_A}{(1-x_A)^2} = c_{A0}k\tau$
Concurrent $A \xrightarrow{k_1} R$	1	$-\frac{dc_A}{d\tau} = k_1c_A + k_2c_A$	$c_A = c_{A0}e^{-(k_1+k_2)\tau}$	$c_A = \frac{c_{A0}}{1+(k_1+k_2)\tau}$
$A \xrightarrow{k_2} S$		$\frac{dc_R}{d\tau} = k_1c_A$	$c_R = \left(\frac{k_1}{k_1+k_2}\right)c_{A0}[1-e^{-(k_1+k_2)\tau}]$	$c_R = \frac{k_1\tau c_{A0}}{1+(k_1+k_2)\tau}$
		$\frac{dc_S}{d\tau} = k_2c_A$	$c_S = \left(\frac{k_2}{k_1+k_2}\right)c_{A0}[1-e^{-(k_1+k_2)\tau}]$	$c_S = \frac{k_2\tau c_{A0}}{1+(k_1+k_2)\tau}$

Table IV-3 (continued)

Reaction	Order	Basic differential equation	Plug-flow reactor	Well-stirred reactor
Consecutive $A \xrightarrow{k_1} R \xrightarrow{k_2} S$	1	$-\frac{dc_A}{d\tau} = k_1 c_A$ $\frac{dc_R}{d\tau} = k_1 c_A - k_2 c_R$ $\frac{dc_S}{d\tau} = k_2 c_R$	$c_A = c_{A0} e^{-k_1 \tau}$ $c_R = \frac{1}{\frac{k_2}{k_1} - 1} \cdot c_{A0}\left(e^{-k_1\tau} - e^{-k_2\tau}\right)$ $c_S = c_{A0} - c_A - c_R$ $\frac{c_{R\max}}{c_{A0}} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}}$ $\tau_{\max} = \frac{\ln k_2/k_1}{k_2 - k_1}$	$c_A = \frac{c_{A0}}{1 + k_1\tau}$ $c_R = \frac{k_1 \tau c_{A0}}{(1+k_1\tau)(1+k_2)\tau}$ $c_S = c_{A0} \frac{k_1 k_2 \tau^2}{(1+k_1\tau)(1+k_2\tau)}$ $\frac{c_{R\max}}{c_{A0}} = \frac{1}{\left[\left(\frac{k_2}{k_1}\right)^{1/2} + 1\right]^2}$ $\tau_{\max} = \frac{1}{\sqrt{k_2 k_1}}$
Mixed $A + B \xrightarrow{k_1} R$ $R + B \xrightarrow{k_2} S$	1	$\frac{dc_A}{d\tau} = -k_1 c_A c_B$ $\frac{dc_B}{d\tau} = -k_1 c_A c_B - k_2 c_R c_B$ $\frac{dc_R}{d\tau} = k_1 c_A c_B - k_2 c_R c_B$ $\frac{dc_3}{d\tau} = k_1 c_B c_R$	$c_R = \frac{c_{A0}}{1 - k_2/k_1}\left[\left(\frac{c_A}{c_{A0}}\right)^{\frac{k_2}{k_1}} - \frac{c_A}{c_{A0}}\right] + c_{R0}\left(\frac{c_A}{c_{A0}}\right)^{\frac{k_2}{k_1}}$; $\frac{k_2}{k_1} \neq 1$ $c_R = c_A\left(\frac{c_{R0}}{c_{A0}} - \ln\frac{c_{A0}}{c_A}\right)$; $\frac{k_2}{k_1} = 1$ $c_{A0} + c_{R0} + c_{S0} = c_A + c_R + c_S$ $\Delta c_A + \Delta c_R + \Delta c_S = 0$ $\Delta c_B + \Delta c_R + 2\,\Delta c_S = 0$	$c_A = c_{A0} - \tau(k_1 c_A c_B)$ $c_R = c_{R0} - \tau(k_2 c_R c_B - k_1 c_A c_B)$ $c_R = \frac{c_A(c_{A0} - c_A + c_{R0})}{c_A + \frac{k_2}{k_1}(c_{A0} - c_A)}$ $c_{A0} + c_{R0} + c_{S0} = c_A + c_R + c_S$

Dividing Eq. (IV-77) into Eq. (IV-76) gives the rate of formation of S relative to that of R:

$$w_{rS}/w_{rR} = (k_2/k_1)c_A^{a_2-a_1} \qquad \text{(IV-78)}$$

An increase or decrease in the right-hand side of the above equation will bring about an increase or decrease in the ratio S/R.

Equation (IV-78) shows that only one variable, c_A, can affect the value of the left-hand side of the equation, because k_1, k_2, a_1 and a_2 are constant for a given system at a given temperature.

It is obvious that in order to secure a high yield, c_A must be maintained as low as practicable. This can be done in any one of the following ways: by using a well-stirred reactor in which the reactant concentration attains the low exit value instantaneously; by using a recycle as a way of reducing the inlet concentration and the concentration of reactant A in the reactor; by bringing down the pressure or raising the inert impurity content in the case of gas-phase systems.

Conversely, if S were the wanted product, its yield could be raised by keeping the reactant concentration, c_A, high. This could be done in any one of the following ways: by using a plug-flow reactor where c_A is brought down gradually from the high inlet value to the low outlet value; by raising the overall pressure in the case of gas-phase systems or by eliminating inert impurities from the feed, thereby raising the reactant concentration at the inlet to the reactor; or by eliminating the product recycle.

The kinetic parameters affect the breakdown of reaction products as follows:

(1) If $a_1 > a_2$, or the reaction order with respect to the wanted product is higher than it is with respect to the unwanted product, then (a_2-a_1) is negative. From Eq. (IV-78) it follows that the ratio S/R will be low at high values of c_A. If, under the circumstances, the process be conducted in a plug-flow reactor, the conditions will be more favourable for the formation of the wanted product, R, and a minimum-sized reactor will be needed.

(2) If $a_1 < a_2$, or the reaction order with respect to the wanted product is lower than it is with respect to the unwanted product, lower reactant concentrations are necessary to make the formation of R predominant. As a result, a large-size reactor will be needed. In such a situation, an optimum design can be obtained by economically balancing the cost of unwanted product recovery against the heavy capital outlays for operations entailed by the larger plant.

(3) If $a_1 = a_2$, that is, if the reaction order is the same with respect to both the wanted and unwanted products, Eq. (IV-78) takes the form

$$w_{rS}/w_{rR} = dc_S/dc_R = k_2/k_1 = \text{constant} \qquad \text{(IV-79)}$$

In other words, the product breakdown remains unchanged at a given ratio of the rate constants, k_2/k_1, and independent of type of reactor.

The product breakdown can be controlled by varying the ratio k_2/k_1

through changes in the process temperature if the two reactions differ in activation energy, or by using a selective catalyst.

An analysis has shown that for simultaneous reactions the product breakdown obeys the following rules:

— for reactions of the same order, the product breakdown is independent of reactor type and concentrations of reacting components;

— for reactions of different orders, a high concentration is preferable in a high-order reaction, and a low concentration in a low-order reaction.

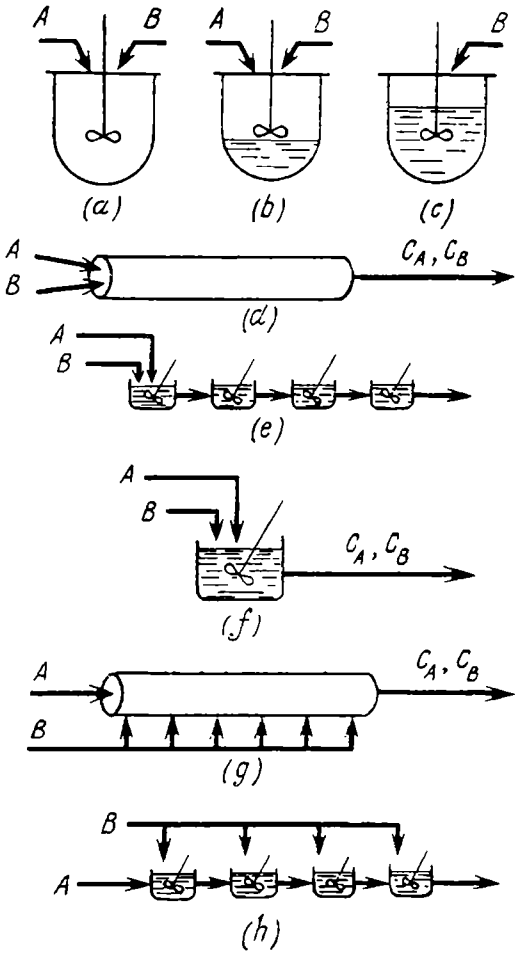


Fig. IV-9. Arrangement of streams in various reactors

(*a*) both reactants are fed simultaneously before reaction (c_A and c_B are high); (*b*) both reactants are fed at a slow rate, after the reaction is allowed to reach completion after each addition (c_A and c_B are high); (*c*) *A* is fed at once, *B* is fed gradually (c_A is high, c_B is low); (*d*) plug-flow reactor (c_A and c_B are high); (*e*) cascade of reactors; (*f*) well-stirred reactor (c_A and c_B are high); (*g*) plug-flow reactor with feed admitted in the course of process (c_A is high, c_B is low); (*h*) cascade with feed to each reactor

Hence, the desired product breakdown can conveniently be maintained by controlling the concentrations of the reacting components. This involves a proper organization of the feed stream. Some of the stream schemes are shown in Fig. IV-9. With a batch or semi-batch reactor, the conditions under which the feed is admitted may be changed as desired. With a conti-

nuous reactor, the process can be conducted, using high concentrations of reactants A and B; this can be best done in a plug-flow reactor. To keep the concentrations of A and B to a minimum, it will be a good plan to use a well-stirred reactor. As an alternative, the concentration of one reacting component may be held high and that of the other low, that is, reactant A may be admitted continuously and reactant B intermittently.

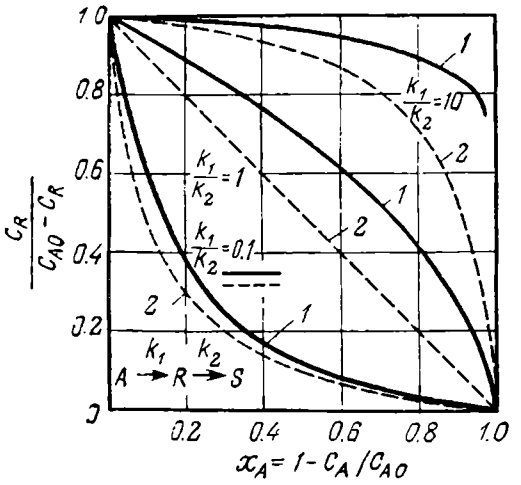


Fig. IV-10. Comparison of plug-flow and well-stirred reactors for consecutive reactions
1 — plug-flow reactor; *2* — well-stirred reactor

The relative yields of the wanted product, R, as a function of kinetic parameters and reactor type for consecutive reactions proceeding according to the scheme $A \xrightarrow{k_1} R \xrightarrow{k_2} S$ are plotted in Fig. IV-10. It is seen that, firstly, the yield of the intermediate reaction product R is always higher from a plug-flow than from a well-stirred reactor; secondly, at high ratios k_1/k_2 the conversion is high while at low ratios it is low; hence, the need for recycling may be considered.

The methods of analysis presented above can readily be implemented on analog computers. In fact, there is quite a number of problem set-ups for typical chemical reactions and for optimum product yields.[5]

IV-5. YIELD, SELECTIVITY AND FRACTIONAL CONVERSION OF VARIOUS REACTORS

Consider a reaction proceeding according to the scheme:

$$\alpha A + \beta B \rightarrow rR + sS$$

The *yield* of the wanted product (say, R) is defined as its fraction in terms of the reactant:

$$\Phi_R = r(R)/\alpha(A) = c_R/c_{A0} \qquad \text{(IV-80)}$$

where α and r are the stoichiometric coefficients, c_R is the concentration of the wanted product, and c_{A0} is the inlet concentration of the reactant.

Selectivity is defined as the ratio of the wanted product to the amount of the reactant that has undergone chemical change:

$$\varphi_R = c_R/(c_{A0} - c_A) \qquad \text{(IV-81)}$$

As before (see p. 281), the *fractional conversion* is the fraction of a reactant that has undergone chemical change:

$$x_A = (c_{A0} - c_A)/c_{A0}$$

The three quantities are related to one another as follows: – for a well-stirred reactor:

$$\Phi_R = c_R/c_{A0} = [c_R/(c_{A0}-c_A)]\,[(c_{A0}-c_A)/c_{A0}] = \varphi_R x_A \qquad \text{(IV-82)}$$

– for a plug-flow or a batch reactor:

$$\Phi_R = \frac{1}{(A)}\int_0^{(A)} \Phi_R\, d(A) = -\frac{1}{c_{A0}}\int_{c_{A0}}^{c_A} \Phi_R\, dc_A = \int_0^{x_A} \Phi_R\, dx_A \qquad \text{(IV-83)}$$

– for a cascade of well-stirred reactors:

$$\Phi_R = \frac{1}{(A)}\sum_{i=1}^{N} \Phi_{R,i}\,\Delta(A)_i = \frac{1}{c_{A0}}\sum_{i=1}^{N} \Phi_{R,i}(c_{Ai}-c_{A,i-1})$$

$$= \sum_{i=1}^{N} \Phi_{R,i}(x_A)_i \qquad \text{(IV-84)}$$

The type of reactor that will give a maximum yield, Φ_R, can readily be selected from the plot of selectivity φ_R as a function of the fractional conversion, x_A (Fig. IV-11). In such a plot, the yield obtained from a plug-flow and a batch reactor is represented by the area under the curve between x_{A0} and x_A. The yield from a well-stirred reactor is represented by the area of a rectangle whose upper right corner touches the selectivity curve and whose base is equal to the difference in the desired fractional conversions.

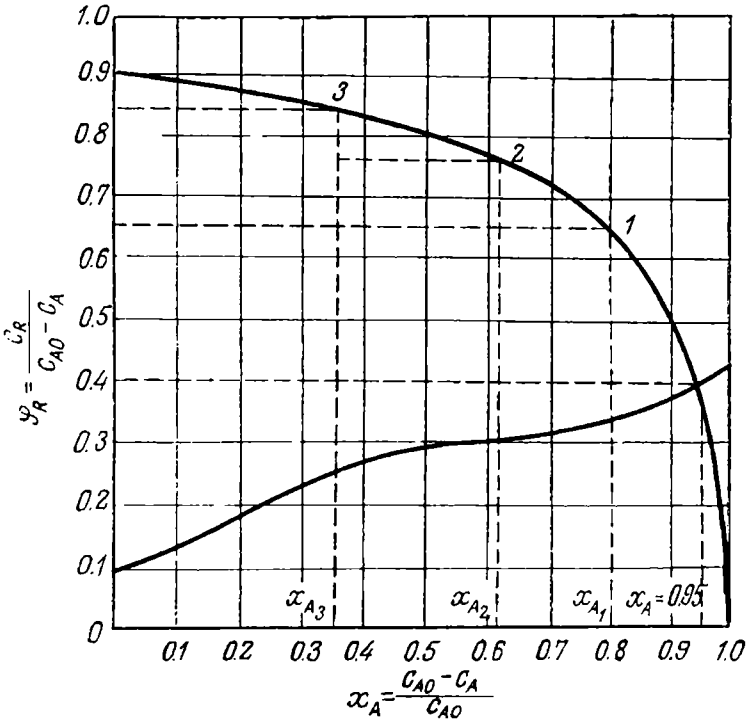


Fig. IV-11. Selectivity as a function of fractional conversion

For a cascade of well-stirred tank reactors, the yield is numerically equal to the sum of the areas of rectangles each of which has a width $x_{Ai}-x_{A,i-1}$ and touches the selectivity curve at the ordinate of φ_{Ri}, where R is the wanted product. The maximum area represents an optimum yield.

As selectivity decreases with increasing fractional conversion (the top curve in the plot of Fig. IV-11), the plug-flow reactor will have the greater area under the curve. In cases where selectivity increases (the bottom curve in the plot of Fig. IV-11), the greater yield will be secured from a well-stirred reactor. In a cascade, the yield can be maximized by appropriately adjusting the fractional conversion for a specified number of units until the total area of rectangles is a maximum.

The relative area of the rectangles representing well-stirred reactors may have one of two meanings. For slow reactions, the reacting components should be admitted to the first reactor at the head of the cascade; in this case the relative area of the rectangles represents the relative reactor hold-up or residence times securing a maximum yield. For fast reactions, one component should be fed into the first reactor of an equal-size reactor cascade; now, the relative area of the rectangles represents the fraction of the reactant that should be admitted into each reactor.

At the peak of the selectivity curve, one may select an optimum combination of plug-flow and well-stirred reactors and an optimum relative conversion, relative residence time or stream feed for each reactor (see p. 176).

IV-6. PLUG FLOW AND COMPLETE MIXING OR COMPLETE MIXING AND PLUG FLOW IN SERIES. SHORT-CIRCUITING

Now we shall consider the effect of plug flow and complete mixing parameters on the fraction conversion for simple hybrid models.[7, 8]

Plug flow and complete mixing in series (the $b-m$ model). The reacting components first pass through a plug-flow region, then through a well-mixed region (Fig. IV-12*a*).

Designating the volume fraction occupied by the well-mixed region as m, the volume of that region may be described as mV_R and that of the plug-flow region as $(1-m)V_R$. Then the following equation will apply to the plug-flow region:

$$(1-m)(V_R/V_q) = -\int_{c_{A0}}^{c_A} dc_A/w_{rb} \qquad \text{(IV-85)}$$

Similarly, for the well-mixed region:

$$c_{A1}-c_{Ak} = w_{rm}mV_R/V_q \qquad \text{(IV-86)}$$

Assuming that c_A represents the theoretically attainable exit concentration for the plug-flow reactor, we may solve the two above equations simultaneously.

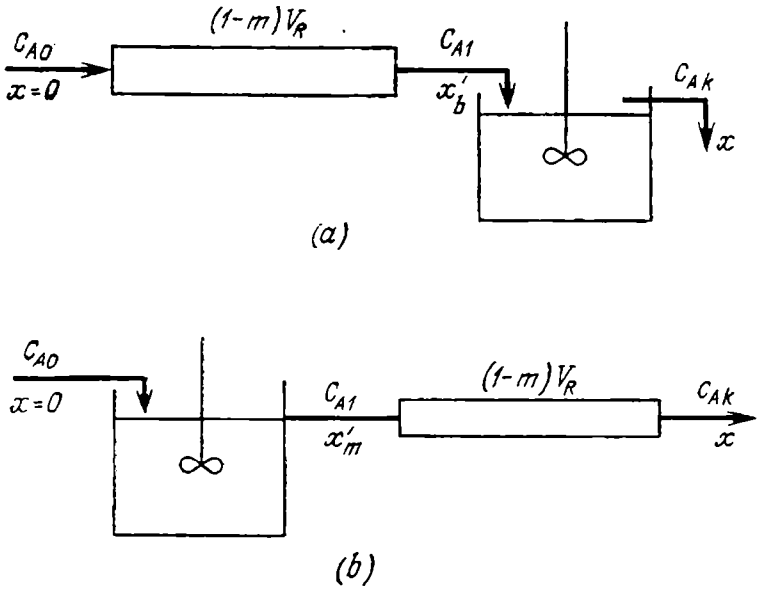


Fig. IV-12. Hybrid reactor models

(*a*) plug flow – complete mixing ($b-m$) model; (*b*) complete mixing – plug flow ($m-b$) model

For a first-order reaction we have

$$c_{A0}/c_{Ab} = (1+m \ln c_{A0}/c_{A1})\,(c_{A0}/c_{A1})^{1-m} \tag{IV-87}$$

$$x = 1-\frac{(1-x_b)^{1-m}}{1-\ln(1-x_b)^m} \tag{IV-88}$$

For a second-order reaction, we have

$$m = \frac{x_b-x}{2x_b(1-x)}\left[1+\sqrt{1+4\frac{1+x_b}{x_b-x}}\right] \tag{IV-89}$$

where x_b is the fractional conversion computed on the assumption of a plug flow.

For a second-order reaction with two reacting components, proceeding according to the scheme

$$A+B \rightarrow \text{product}$$

we may write:

$$(1-x)\left[(M-1)+(M-x)\ln\left(\frac{M-x_b}{M(1-x_b)}\right)^m\right] = \frac{(M-1)^2}{M\left[\dfrac{M-x_b}{M(1-x_b)}\right]^{1-m}} \tag{IV-90}$$

where $M = c_{B0}/c_{A0}$.

For a third-order reaction,

$$m^3 - \left\{\frac{4\left[0.25\left(\frac{c_{A0}}{c_A}\right)^2-\left(\frac{c_{A0}}{c_{Ak}}\right)^2\right]}{(c_{A0}/c_A)^2-1}\right\}m^2 - \left\{\frac{4\left(\frac{c_{A0}}{c_{Ak}}\right)^2\left[\left(\frac{c_{A0}}{c_A}\right)^2-\left(\frac{c_{A0}}{c_{Ak}}\right)^2\right]}{\left[\left(\frac{c_{A0}}{c_A}\right)^2-1\right]^2}\right\}m$$

$$-\left\{\frac{4\left(\frac{c_A}{c_{Ak}}\right)^4\left[\left(\frac{c_A}{c_{A0}}\right)^2-\left(\frac{c_{A0}}{c_{Ak}}\right)^2\right]}{\left[\left(\frac{c_{A0}}{c_A}\right)^2-1\right]^3}\right\} = 0 \tag{IV-91}$$

For zero-order reactions, $x = x_b$, irrespective of m, and, as a consequence, the fractional conversion is solely decided by the total residence time.

Changes in the fractional conversion and the fraction of the well-mixed region for reactions of various orders in reactors operating under conditions of plug flow and complete mixing in series (the $b-m$ model) are shown in the plot of Fig. IV-13 on the assumption that the fractional conversion x in a plug-flow reactor would be 90% for the same residence time. As follows from the plot, an increase in m reduces the fractional conversion in comparison with its value for the plug-flow reactor, the reduction being far more pronounced in reactions of higher orders.

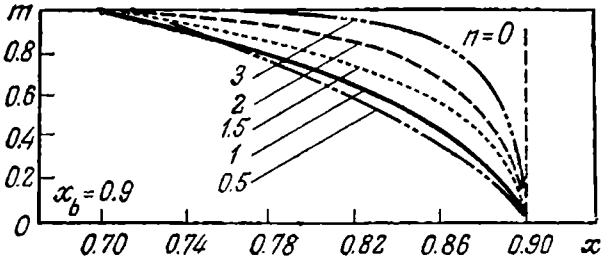


Fig. IV-13. Changes in fractional conversion and fraction of complete-mixing region for a plug flow — complete mixing reactor carrying out various order reactions.

Complete mixing and plug flow in series (the $m-b$ model). Referring to Fig. IV-12*b*, for the well-mixed region we may write

$$c_{A0}-c_{A1} = w_{rm}mV_R/V_q \tag{IV-92}$$

and for the plug-flow region:

$$-\int_{c_{A1}}^{c_{Ak}} dc/w_{rb} = (1-m)V_R/V_q \tag{IV-93}$$

If it were a plug-flow reactor, the inlet and exit concentrations, c_b, would correspond to the time τ_b or V_R/V_q given by Eq. (IV-34). Solving Eqs. (IV-34) and (IV-92) simultaneously, we get

$$c_{A0} = c_b+\frac{m}{n-1}c_{A1}^n(c_b^{1-n}-c_{A0}^{1-n}) \tag{IV-94}$$

Solving Eqs. (IV-34) and (IV-93) simultaneously, we get

$$c_{A1}^{1-n} = c_{Ak}^{1-n}-(1-m)(c_b^{1-n}-c_{A0}^{1-n}) \tag{IV-95}$$

Combining the last equation with Eq. (IV-92), we obtain the sought solution.

For a second-order reaction we may write

$$m = \frac{(c_{A0}/c_B-c_{A0}/c_{Ak})+\sqrt{c_{A0}/c_B-c_{A0}/c_{Ak}}}{c_{A0}/c_B-1} \tag{IV-96}$$

$$m = \frac{x_b-x}{x_b(1-x)}+\sqrt{\left[\frac{x_b-x}{x_b(1-x)}\right]\left[\frac{1-x_b}{x_b}\right]} \tag{IV-97}$$

For a second-order reaction proceeding to the scheme $A+B \rightarrow$ product, we obtain:

$$\frac{M}{M-1}\left\{1-\frac{1-x}{M-x}\left[\frac{x-x_b}{M(1-x_b)}\right]^{1-m}\right\}^2 = 1+\frac{1-x}{M-x}\left\{\ln\left[\frac{M-x_b}{M(1-x_b)}\right]^m-1\right\}\left[\frac{M-x_b}{M(1-x_b)}\right]^{1-m} \quad \text{(IV-98)}$$

For a zero-order reaction the result is the same as with plug flow and complete mixing in series (the $b-m$ model), because $x = x_b$ is independent of amount of mixing.

For reactions of other orders we may write:

at $n = 0.5$

$$m = \frac{\sqrt{\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1\right]\left\{\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1+2\left(\frac{c_{A0}/c_b}{c_{A0}/c_{Ak}}\right)^{0.5}\right]-\left(\frac{c_{A0}/c_{Ak}-1}{c_{A0}/c_{Ak}}\right)\frac{c_{A0}}{c_b}\right\}}}{\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1} \quad \text{(IV-99)}$$

at $n = 1.5$

$$m^3-3\left[\frac{(c_{A0}/c_b)^{0.5}-1-(c_{A0}/c_{Ak})^{0.5}}{(c_{A0}/c_b)^{0.5}-1}\right]m^2 + 3m\left\{\frac{\left(\frac{c_{A0}}{c_{Ak}}-1\right)-\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1\right]\left[2\left(\frac{c_{A0}}{c_{Ak}}\right)^{0.5}-\left(\frac{c_{A0}}{c_b}\right)^{0.5}+1\right]}{\left[\left(\frac{c_{A0}}{c_b}\right)^{0,5}-1\right]^2}\right\}$$

$$-\left\{\frac{\left(3\frac{c_{A0}}{c_{Ak}}-1\right)\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1\right]+\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1-3\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1\right]^2\left(\frac{c_{A0}}{c_{Ak}}\right)^{0.5}\left(\frac{c_{A0}}{c_{Ak}}-1\right)}{\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1\right]^3}\right\} = 0 \quad \text{(IV-100)}$$

at $n = 3$

$$m^3-3\left[\frac{(c_{A0}/c_b)^2-(c_{A0}/c_{Ak})^2-0.25}{\left(\frac{c_{A0}}{c_b}\right)^2-1}\right]m^2 + 3\left\{\frac{\left[\left(\frac{c_{A0}}{c_b}\right)^2-1\right]\left[\left(\frac{c_{A0}}{c_b}\right)^2-2\left(\frac{c_{A0}}{c_{Ak}}\right)^2\right]\left[+\left(\frac{c_{A0}}{c_{Ak}}\right)^2-1\right]}{\left[\left(\frac{c_{A0}}{c_b}\right)^{0.5}-1\right]^2}\right\}m$$

$$-\left\{\frac{\left[\left(\frac{c_{A0}}{c_b}\right)^2-1\right]\left\{\left(\frac{c_{A0}}{c_{Ak}}\right)^2\left[3\left(\frac{c_{A0}}{c_{Ak}}\right)^2-2\right]-\left[\left(\frac{c_{A0}}{c_b}\right)^2-1\right]\left[3\left(\frac{c_{A0}}{c_{Ak}}\right)^2-\left(\frac{c_{A0}}{c_b}\right)^2\right]\right\}-\left(\frac{c_{A0}}{c_{Ak}}\right)^4\left[\left(\frac{c_{A0}}{c_{Ak}}\right)^2-1\right]}{\left[\left(\frac{c_{A0}}{c_b}\right)^2-1\right]}\right\} = 0 \quad \text{(IV-101)}$$

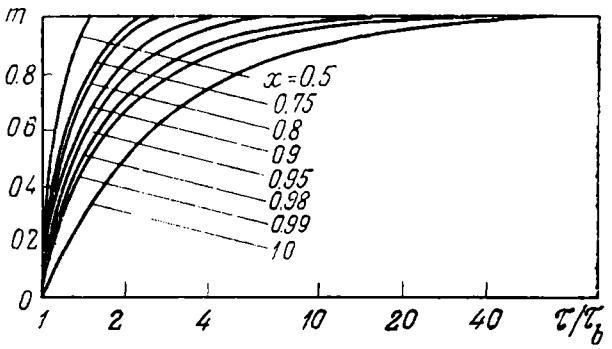


Fig. IV-14. Relative residence time in plug flow — complete mixing ($b-m$) and complete mixing — plug flow ($m-b$) reactors for first-order reactions at various fractional conversions

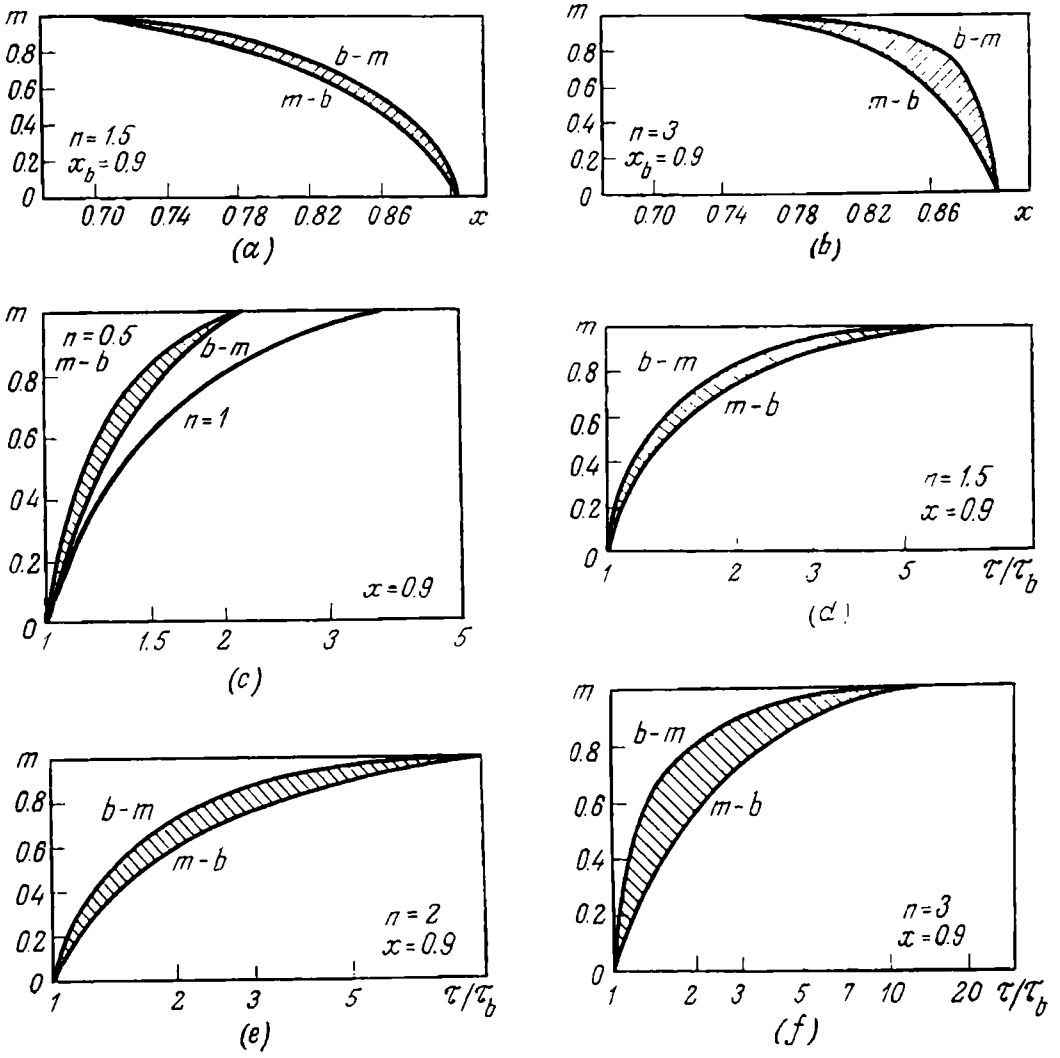


Fig. IV-15. Comparison of plug flow — complete mixing (b—m) and complete mixing — plug flow ($m-b$) reactors

(*a*), (*b*) changes in x with changes in m at residence time corresponding to $x_b = 0.9$ ($n = 1.5$ and $n = 3$); (*c*)–(*f*) changes in relative residence time τ/τ_b with changes in m at $x = 0.9$ for different reaction orders

A comparison of residence times for $(b-m)$ and $(m-b)$ reactors with those for a plug-flow reactor is made in Fig. IV-14 while the plot of Fig. IV-15 compares them in terms of fractional conversion, residence time and the size of the complete mixing region for a given value of x.

Short-circuiting. One speaks of short-circuiting when some reactant passes directly from the inlet to the outlet without reacting with the reactor contents. Short-circuiting is especially troublesome in reactors with a low rate of mixing, when a stagnant zone may well appear.

Figure IV-16 shows a continuous stirred tank reactor with short-circuiting expressed as a fraction, $(1-z)$, of the feed V_q admitted to the reactor, where z is the fraction of the total liquid that enters the reactor and passes through a complete mixing region.

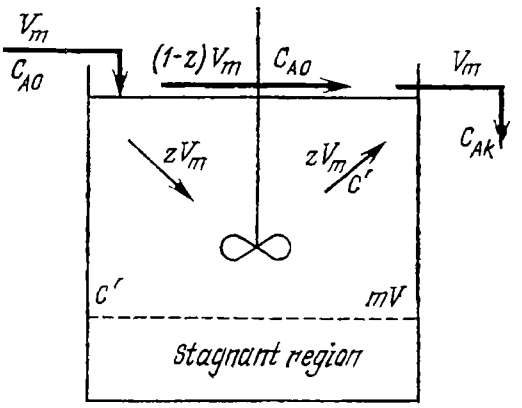


Fig. IV-16. Stirred tank with short-circuiting

Referring to Fig. IV-16, short-circuiting may be described as follows.

The fraction of the complete mixing region is

$$m = \frac{c_{A0}-c_{Ak}}{c_{A0}-c_m}\,\frac{w_{rm}}{w_r} \tag{IV-102}$$

$$w_{rm} = kc_m^n \tag{IV-102a}$$

$$w_r = k(c')^n \tag{IV-102b}$$

From a material balance, the concentration, c', in the complete mixing region is given by

$$c' = \frac{c_{Ak}-(1-z)c_{A0}}{z} \tag{IV-103}$$

Substituting Eqs. (IV-102*a*), (IV-102*b*) and (IV-103) in Eq. (IV-102) gives

$$m = \left(\frac{c_{A0}/c_{Ak}}{c_{A0}/c_m}\right)^{n-1}\left[\frac{(c_{A0}/c_{Ak})\cdot 1}{c_{A0}/c_m-1}\right]\left[\frac{z}{1-(1-z)-c_{A0}/c_{Ak}}\right]^n \tag{IV-104}$$

$$m = \frac{x}{x_m}\left[\frac{z(1-x_m)}{z-x}\right]^n \tag{IV-105}$$

where x_m is the fractional conversion attained in a continuous well-stirred reactor.

From application of Eq. (IV-105) to reactions of various orders, the following may be inferred. At $n = 0$, short-circuiting has no sense

$$m = x/x_m \tag{IV-106}$$

that is, the fractional conversion is solely determined by the size of the complete mixing zone.

At $n = 0.5$,

$$m = \frac{x}{x_m}\sqrt{\left[\frac{z(1-z)}{z-x}\right]} \qquad \text{(IV-107)}$$

At $n = 1$,

$$m = \frac{x}{x_m}\left[\frac{z(1-x_m)}{z-x}\right] \qquad \text{(IV-108)}$$

At $n = 1.5$,

$$m = \frac{x}{x_m}\left[\frac{z(1-x_m)}{z-x}\right]^{1.5} \qquad \text{(IV-109)}$$

At $n = 2$,

$$m = \frac{x}{x_m}\left[\frac{z(1-x_m)}{z-x}\right]^{2} \qquad \text{(IV-110)}$$

At $M = c_{B0}/c_{A0}$,

$$m = \frac{x}{x_m}\,\frac{z^2(1-x_m)\,(M-x_m)}{(zM-x)\,(z-x)} \qquad \text{(IV-111)}$$

At $n = 3$,

$$m = \frac{x}{x_m}\left[\frac{z(1-x_m)}{z-x}\right]^{3} \qquad \text{(IV-112)}$$

Variations in the fractional conversion according to the size of the well-stirred region and short-circuiting for reactions of various orders at $x_m = 0.9$ are shown in the plot of Fig. IV-17.

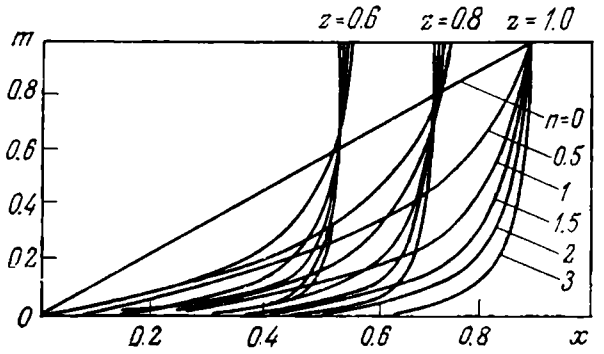


Fig. IV-17. Fractional conversion as a function of size of complete mixing and short-circuiting for different order reactions at a residence time corresponding to $x_m = 0.9$

IV-7. REACTOR DESIGN FROM RESPONSE CURVES WITH ALLOWANCE FOR SYSTEM MACROSTATE

Where a mathematical model is to describe a flow pattern with mixing, equations of reaction kinetics and response curves (system responses) representing the residence times of fluid elements in the reactor prove insufficient. For a proper explanation of the mixing pattern in the reactor, we should also know the *level of mixing*, because this factor has a direct bearing on the progress of chemical change.

Mixing at the microscopic level, or the *microscopic state of a system*, refers to mixing at the level of individual molecules. In this case, around each molecule there are no excess molecules that entered the reactor at the same time as a given molecule. The liquid entering the reactor is dispersed at the molecular level inside a time span which is a small fraction of the mean residence time, τ. The system is chemically homogeneous.

Mixing at the macroscopic level, or the *macroscopic state of a system*, refers to mixing at the level of aggregates of molecules. The liquid entering the reactor is broken up into aggregates which are uniformly distributed throughout the reactor bulk. The system remains completely segregated.

The system state level is decided by the *degree of system segregation*, I. In this connection, one uses the concepts of the *point concentration* and the *point age* of the fluid.[9] The two concepts define the concentration or age averaged over a region very small in comparison not only with the entire system, but also with the size of molecular aggregates, yet sufficiently large to contain many molecules.

Let the age of a molecule be the time, τ, that elapses since the molecule enters the system. Then we can find the age variance of all molecules in the system, that is, the mean square deviation of the molecules' age from the mean age:

$$\operatorname{Var}\tau = \overline{(\tau-\bar{\tau})^2} \qquad \text{(IV-113)}$$

where $\bar{\tau}$ is the mean age of all molecules contained in the system at a given instant (the overscribed bar indicates that the average is taken over all molecules).

If the average age of the molecules at each point be τ_p, then the age variance may serve as a measure of system segregation:

$$\operatorname{Var}\tau_p = \overline{(\tau_p-\bar{\tau})^2} \qquad \text{(IV-114)}$$

where the overscribed bar indicates that the average is taken over all points.

With mixing at the molecular level, the average age of all molecules at each point is the same and equal to the average age of all molecules in the system; then the age variance between the various points is null. With mixing at the macroscopic level, that is, if the system is completely segregated, the age variance between the points in the system is equal to the age variance of all molecules:

$$I = \operatorname{Var}\tau_p/\operatorname{Var}\tau = 1 \qquad \text{(IV-115)}$$

For any other degree of segregation, I will be less than one:

$$I = \operatorname{Var}\tau_p/\operatorname{Var}\tau = \overline{(\tau_p-\bar{\tau})^2}/\overline{(\tau-\bar{\tau})^2} \qquad \text{(IV-116)}$$

The limiting value of $I = 0$ corresponds to a state of maximum mixing.

For a system with a residence time distribution similar to that of a well-stirred reactor, the value of I may lie between zero (mixing at the molecular level) and unity (complete segregation). For a system with plug flow where the fluid elements are not mixed, the degree of segregation has a maximum value of unity ($I = 1$).

It is instructive to trace the effect of the mixing level or the system state on the fractional conversion in various reactors. We shall consider two extreme types of reactor, the plug-flow type and the continuous stirred tank type, connected in series (Fig. IV-18).

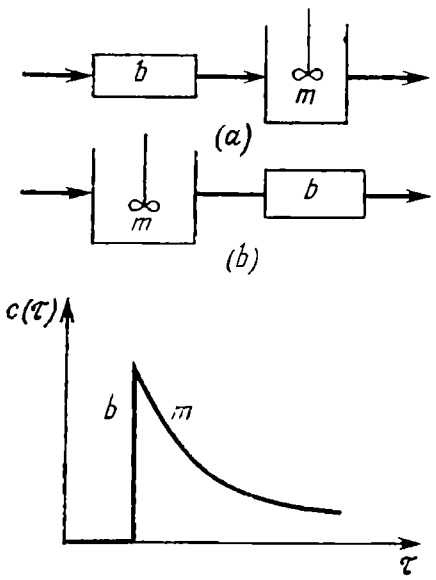


Fig. IV-18. Mixing at (*a*) a later stage and (*b*) an earlier stage

In arrangement "*a*", mixing takes places at a later stage, while in arrangement "*b*" it occurs at an earlier stage. The residence time distribution is the same for both schemes (see Fig. IV-18), being an ordinary impulse response for the plug-flow type (*b*) and an exponential response for the well-stirred type (*m*).

If no chemical reaction takes place in the reactors, that is, if they operate as flow-through units, for, say, smoothing out variations in temperature or concentration in a steady-state stream, their performance will be identical. The situation is different when mixing occurs the same instant as chemical change takes place. Although the overall degree of mixing is the same in both arrangements, mixing in "*b*" takes place at an earlier stage of chemical change, while in "*a*" it occurs at a later stage. Naturally, the yields of the two systems will be different. For a reaction of an order more than unity, proceeding under isothermal conditions the conversion will be greater with arrangement "*a*". According to what has been stated above, the degree of segregation in the plug-flow reactor is greater than it is in the well-stirred reactor ($I_b > I_m$).

In the light of the foregoing, the effect of mixing may be interpreted in a different way.[10] Imagine a complete-segregation reactor as a long tube carrying a plug flow with a great number of side outlets spaced a short distance apart (Fig. IV-19). The stream is tapped at these side outlets so that the overall residence time distribution of the system is equal to the distribution under study. It is also assumed that the volume of the side outlets is negligible.

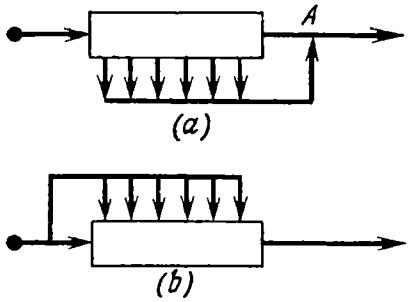


Fig. IV-19. Plug-flow reactor with (*a*) side taps and (*b*) maximum mixing

In such a system, a representative point may be visualized as a very short length of the reactor tube. Obviously, the age distribution at each point is very narrow and there is no mixing in the system, except at the common exit. Thus, molecules of different ages are mixed at the latest possible time, that is, at point *A* (Fig. IV-19*a*).

This completely segregated continuous-flow system can readily be converted to a completely mixed continuous-flow system by simply reversing the stream. Then the system will have a multitude of inlets and one outlet (Fig. IV-19*b*). It is assumed that radial mixing is complete and that the incoming liquid is dispersed along the length of the tube instantaneously. As soon as it enters the system, each molecule is mixed with other molecules which leave the system all at the same time. Thus the molecules are mixed at the earliest possible time. This is a state of maximum mixing, diametrically opposite to a state of complete segregation.

To sum up, in designing a chemical reactor, knowledge is vitally important of (1) reaction kinetics; (2) system response or residence time distribution; (3) macroscopic or microscopic state of the system; and (4) whether mixing takes place at an earlier or later stage.

Classical kinetics deals with chemical change at the microscopic level and, as a consequence, it deals with microsystems. All that has been said about the calculation of chemical change in various types of reactor applies to microsystems. Now we shall consider the calculation of chemical reactors at the macroscopic level for two extreme types, the plug-flow type and the well-stirred type.

Batch reactor (plug flow in time). Consider a batch reactor charged with a fluid in a macroscopic state, containing reactant A. Since each aggregate of molecules behaves as a minute batch reactor of its own, the fractional conversion will be the same in all aggregates, that is, the situation is the same as with a reactor charged with a fluid in a microscopic state. Thus, in batch processes the state of aggregation is not changed and does not affect the degree of conversion or distribution.

Plug-flow reactor. In this case, the stream is completely segregated into aggregates of molecules, and chemical change in each aggregate occurs in the same way as in the previous case. In other words, in a plug-flow reactor chemical change is identically the same, whatever the state of the reaction mixture, microscopic or macroscopic.

Well-stirred reactor. When the fluid is charged into a well-stirred reactor in a macroscopic state, the reactant concentration in aggregates of molecules decreases in the same manner as it does in a batch reactor and does not reach the low exit value at once, as this happens in systems in a microscopic state. The reactant concentration changes with the residence time of the reactant, decided by the impulse response of the reactor.

For a well-stirred reactor, Eq. (II-33) defines the impulse response as

$$C(\tau) = \exp(-\tau/\bar{\tau})/\bar{\tau} \tag{IV-117}$$

On the basis of Eq. (IV-73), the average concentration, $\bar{c}_A$, of reactant A leaving the reactor can be defined as

$$\bar{c}_A/c_{A0} = 1 - x_A = \int_0^\infty (c_A/c_{A0})_{batch} - c(\tau)\, d\tau = \int_0^\infty (c_A/c_{A0})_{batch} \frac{\exp(-\tau/\bar{\tau})}{\tau}\, d\tau \tag{IV-118}$$

Table IV-4

Fraction of Reactant Remaining Unreacted and Fractional Conversion for Macroscopic and Microscopic Systems in Idealized Reactor Models[6]

Reaction order	Plug flow	Complete mixing	
	microscopic or macroscopic state	microscopic state	macroscopic state
0	$\frac{c}{c_0} = 1-\frac{k\tau}{c_0}$ at $\frac{k\tau}{c_0} \leqslant 1$ $c = 0$ at $\frac{k\tau}{c_0} \geqslant 1$	$\frac{c}{c_0} = 1-\frac{k\tau}{c_0}$ at $\frac{k\tau}{c_0} \leqslant 1$ $c = 0$ at $\frac{k\tau}{c_0} \geqslant 1$	$\frac{c}{c_0} = 1-\frac{k\tau}{c_0}+\frac{k\tau}{c_0}\,e^{-\frac{c_0}{k\tau}}$
$^1/_2$	$\frac{k\tau}{c_0^2} = 2(1-\sqrt{1-x})$	$\frac{k\tau}{c^{1/2}} = \frac{x}{\sqrt{1-x}}$	$x = \frac{k\tau}{c_0^{1/2}}-\frac{1}{2}\cdot\frac{k^2\tau^2}{c_0}+\frac{1}{2}\cdot\frac{k^2\tau^2}{c_0}\,e^{-\frac{2c_0^{1/2}}{k\tau}}$; $0 \leqslant \frac{k\tau}{c_0^{1/2}} \leqslant 2$
1	$\frac{c}{c_0} = e^{-k\tau}$; $k\tau = \ln\frac{1}{1-x}$	$\frac{c}{c_0} = \frac{1}{1+k\tau}$; $k\tau = \frac{x}{1-x}$	$\frac{c}{c_0} = \frac{1}{1+k\tau}$; $k\tau = \frac{x}{1-x}$
2	$\frac{c}{c_0} = \frac{1}{1+c_0k\tau}$; $kc_0\tau = \frac{x}{1-x}$	$\frac{c}{c_0} = \frac{-1\pm\sqrt{1+4c_0k\tau}}{2c_0k\tau}$; $kc_0\tau = \frac{x}{(1-x)^2}$	$\frac{c}{c_0} = -\frac{e^{1/c_0k\tau}}{c_0k\tau}\,Ei\left(-\frac{1}{c_0k\tau}\right)$; $Ei\left(-\frac{1}{c_0k\tau}\right)$ = exponential integral $x = 1-e^{1/c_0k\tau}Ei\left(-\frac{1}{c_0k\tau}\right)$
n	$\frac{c}{c_0} = [1+(n-1)c_0^{n-1}k\tau]^{\frac{1}{1-n}}$ $x = 1-[1+(n-1)c_0^{n-1}k\tau]^{\frac{1}{1-n}}$	$\left(\frac{c}{c_0}\right)^n c_0^{n-1}k\tau+\frac{c}{c_0}-1 = 0$ $x = \frac{c^n}{c_0}k\tau$	$\frac{c}{c_0} = \frac{1}{\tau}\int_0^\infty [1(n-1)c_0^{n-1}k\tau]^{\frac{1}{1-n}}\,e^{\frac{\tau}{\bar{\tau}}}\,d\tau$

where $(c_A/c_{A0})_{batch}$ is the ratio of the final to initial concentration of reactant A in a batch reactor.

Equation (IV-118) may be used to determine the fractional conversion in the macroscopic state for a first-order reaction. As before, for a batch (plug-flow) reactor (see Table IV-3) we have

$$(c_A/c_{A0})_{batch} = \exp(-k\tau) \tag{IV-119}$$

Substituting Eq. (IV-119) in Eq. (IV-118) gives

$$\bar{c}_A/c_{A0} = \frac{1}{\bar{\tau}} \int_0^\infty \exp(-k\tau) \exp(-\tau/\bar{\tau})\, d\tau \tag{IV-120}$$

Hence, on integration,

$$\bar{c}_A/c_{A0} = 1/(1+k\bar{\tau}) \tag{IV-121}$$

which agrees with the equation for a well-stirred reactor in a microscopic state (see Table IV-4).

Thus, for linear systems (first-order reactions), the degree of segregation, I, has no effect on the fractional conversion, that is, a well-stirred reactor will give the same yield with both microscopic and macroscopic systems.

However, whether a system is in microscopic or macroscopic state is important for non-linear systems in a well-stirred reactor (see Table IV-4 and Fig. IV-20).

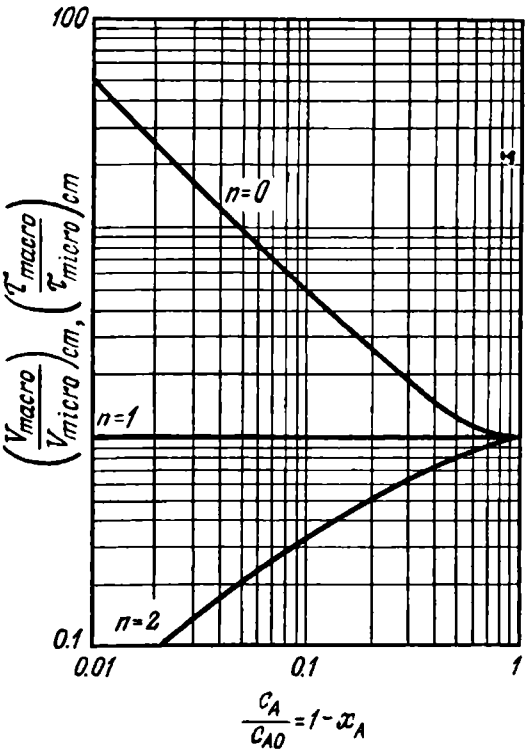


Fig. IV-20. Effect of mixing level on the volume of a well-stirred reactor for different order reactions

Referring to Fig. IV-20, to obtain the same fractional conversion a bigger well-stirred reactor will be needed for a macroscopic than a microscopic system in reactions of an order less than unity, the reverse being true of reactions of an order greater than unity. To state this differently, an increase in segregation improves the effectiveness of a well-stirred reactor for reactions of an order greater than unity and impairs it for reactions of an order less than unity. If the impulse response of a real reactor is very close to that of the ideal plug-flow model, the degree of segregation will have no effect on the fractional conversion.

The foregoing may be summed up as follows:

(1) Consideration of the degree of segregation or amount of mixing is important only for homogeneous systems, because heterogeneous systems are always completely segregated, that is, they are always in a macroscopic state.

(2) Consideration of the degree of segregation or amount of mixing is important only for continuous stirred tank reactors, because the streams in reactors operating under plug-flow conditions are always completely segregated, that is, they are in a macroscopic state or, which is the same, the fluid molecules are mixed at once on entering the plug-flow reactor owing to radial mixing.

(3) For first-order homogeneous reactions in continuous stirred tank reactors the fractional conversion is independent of the level of mixing. With a completely segregated state, the average rate of reaction is higher for orders greater than unity and lower for orders lower than unity.

(4) The fractional conversion is always greater in plug-flow than in continuous well-stirred reactors at both minimum and maximum segregation.

(A) DESIGN EQUATIONS FOR A CASCADE WITH DIFFERENT LEVELS OF MIXING

As an example, we shall take a reaction of the type $A \rightarrow$ products under isothermal conditions (the fluid is assumed to be at constant density).[11] From a material balance under steady-state conditions, we may write the following dimensionless relations for any mth reactor in a cascade:

$$x_m = k_m(c_{A0})^{n-1}\tau_m \qquad \text{(batch reactor)} \qquad \text{(IV-122)}$$

$$x_m = k_m(c_{A0})^{n-1}\,(l/w)_m \qquad (m \text{ continuous-flow reactors}) \qquad \text{(IV-123)}$$

$$l/w = V_R/V_q \qquad \text{(stirred-tank reactors)} \qquad \text{(IV-124)}$$

$$y_m = c_{Am}/c_{A0} \qquad \text{(dimensionless concentration)} \qquad \text{(IV-125)}$$

For reactions of an order other than unity ($n \neq 1$), the following relations may be written:

1. *Plug flow or batch reactor*

$$-dy_m/dx_m = (y_m)^n \qquad \text{(IV-126)}$$

$$-\int_{y_{m-1}}^{y_m} dy_m/(y_m)^n = \int_0^{x_m} dx_m \qquad \text{(IV-127)}$$

whence

$$1/x_m(y_m)^{n-1} = (n-1)+1/x_m(y_{m-1})^{n-1} \qquad \text{(IV-128)}$$

2. Complete microscopic mixing

$$y_{m-1}-y_m = x_m(y_m)^n \qquad \text{(IV-129)}$$

or

$$[x_m(y_m)^{n-1}+1]^{n-1}\, x_m(y_m)^{n-1} = x_m(y_{m-1})^{n-1} \qquad \text{(IV-130)}$$

3. Complete macroscopic mixing (segregated mixing)

$$[x_m(\bar{y}_m)^{n-1}]^{1/(n-1)} = \int_0^\infty \{[x_m(y_m)^{n-1}]_{batch}^{1/(n-1)}\}\, e(\tau)\, d\tau \qquad \text{(IV-131)}$$

where $\bar{y}_m$ is the average dimensionless concentration for microscopic batch reactors ($\overline{c/c_0}$), and $e(\tau)$ is the exit residence time distribution function for a well-stirred reactor.

Hence,

$$[x_m(\bar{y}_m)^{n-1}]^{1/(n-1)}$$

$$= \int_0^\infty \{[x_m(y_{m-1})^{n-1}(w\tau/l)]^{-1}+n-1\}^{-1/(n-1)} \exp(-w\tau/l)\, d(w\tau/l) \qquad \text{(IV-132)}$$

With segregated mixing, the time needed for complete conversion in each microscopic batch reactor has an upper limit. For reactions of an order less than unity, it may be found from the rate equation as the time in which the concentration drops to zero, or

$$(\tau_{max})_m = \frac{(c_{A(m-1)})^{1-n}}{(1-n)k_m} \qquad \text{(IV-133)}$$

Putting $z = w\tau/l$, then

$$(z_{max})_m = \left(\frac{w\tau_{max}}{l}\right)_m = \frac{(y_{m-1})^{1-n}}{(1-n)\, x_m[x_m(\bar{y}_m)]^{1/(n-1)}}$$

$$= \int_0^{(z_{max})_m} \{[x_m(y_{m-1})^{n-1}z]^{-1}+n-1\}^{-1/(n-1)} \exp(-z)\, dz \qquad \text{(IV-134)}$$

For a zero-order reaction, $(z_{max})_m = y_{m-1}/x_m$. Then, on integration and multiplication, we get

$$\frac{y_m}{x_m} = \exp\left[-\frac{y_{m-1}}{x_m}\right]-1+\frac{y_{m-1}}{x_m} \qquad \text{(IV-135)}$$

4. Segregated laminar flow (no radial diffusion)

The residence time distribution of material in the reactor exit stream is

$$e(\tau) = 1/2(w\tau/l)^{-3}d(w\tau/l) = 1/2(z^{-3}\, dz) \qquad \text{(IV-136)}$$

Design Equations of a Cascade of Reactors with Different Levels of Mixing

Reaction order, n	Plug flow or batch reactor	Complete microscopic mixing	Complete macroscopic mixing	Segregated laminar flow (no radial diffusion)
$n = 0$ $\frac{1}{x_m(y_m)^{-1}}$	$\frac{1}{x_m(y_{m-1})^{-1}} - 1$ $x_m(y_{m-1})^{-1} < 1$	$\frac{1}{x_m(y_{m-1})^{-1}} - 1$ $x_m(y_{m-1})^{-1} < 1$	$\exp\left[\frac{-1}{x_m(y_{m-1})^{-1}}\right] - 1 + \frac{1}{x_m(y_{m-1})^{-1}}$	$\frac{x_m(y_{m-1})^{-1}}{4} + \frac{1}{x_m(y_{m-1})^{-1}} - 1$ $x_m(y_{m-1})^{-1} < 2$
$n = \frac{1}{2}$ $\frac{1}{x_m(y_m)^{-0.5}}$	$\frac{1}{x_m(y_{m-1})^{-0.5}} - 0.5$ $x_m(y_{m-1})^{-0.5} < 2$	$-\frac{1}{2} + \left\{\frac{1}{4} + \frac{1}{[x_m(y_{m-1})^{-0.5}]^2}\right\}^{1/2}$	$\left\{\frac{1}{[x_m(y_{m-1})^{-0.5}]^2} - \frac{1}{x_m(y_{m-1})^{-0.5}} + \frac{1}{2}\left(1 - \exp\left[\frac{-2}{x_m(y_{m-1})^{-0.5}}\right]\right)\right\}^{1/2}$	$\left\{\frac{1}{[x_m(y_{m-1})^{-0.5}]^2} - \frac{1}{x_m(y_{m-1})^{-0.5}} + \frac{1}{8}\ln\left[\frac{4}{x_m(y_{m-1})^{0.3}}\right] + \frac{3}{16}\right\}^{1/2}$
$n = 1$ y_m/y_{m-1}	$\exp(-x_m)$	$1/(1+x_m)$	$1/(1+x_m)$	$(x_m/2)^2[-\mathrm{Ei}(-x_m/2)]$
$n = 2$ $x_m y_m$	$\frac{x_m y_{m-1}}{(x_m y_{m-1}) + 1}$	$-\frac{1}{2} + \left[\frac{1}{4} + x_m y_{m-1}\right]^{1/2}$	$\exp\left(\frac{1}{x_m y_{m-1}}\right)\left[-\mathrm{Ei}\left(\frac{-1}{x_m y_{m-1}}\right)\right]$	$(x_m y_{m-1})^3 \ln\left[\frac{2 + (x_m y_{m-1})}{x_m y_{m-1}}\right]^{1/2} - (x_m y_{m-1})^2 + x_m y_{m-1}$

Then,

$$[x_m(\bar{y}_m)^{n-1}]^{1/(n-1)} = \int_{\tau_0}^{\infty} \{[x_m(y_m)^{n-1}]_{batch}\}^{1/(n-1)} e(\tau)\, d\tau \qquad \text{(IV-137)}$$

where $\tau_0 = l/2w$ is the minimum residence time corresponding to the maximum velocity at the centre of the tube.

Introducing the variable $z = w\tau/l$, we get

$$[x_m(\bar{y}_m)^{n-1}]^{1/(n-1)} = 1/2 \int_{1/2}^{z_{max}} \{[x_m(\bar{y}_{m-1})^{n-1}z]^{-1} + n - 1\}^{-1/(n-1)} z^{-3}\, dz \qquad \text{(IV-138)}$$

The design equations obtained by integration of the expression discussed above are summarized in Table IV-5.

As follows from the table, the ratio y_m/y_{m-1} is a function of only x_m. Therefore, the final value, y_f, after k stages of a cascade may be obtained by simply multiplying through the y-ratios found for each x_m.

Plots which may be useful in the design of a cascade of reactors with different mixing patterns are given in Figs. IV-21 through IV-24.

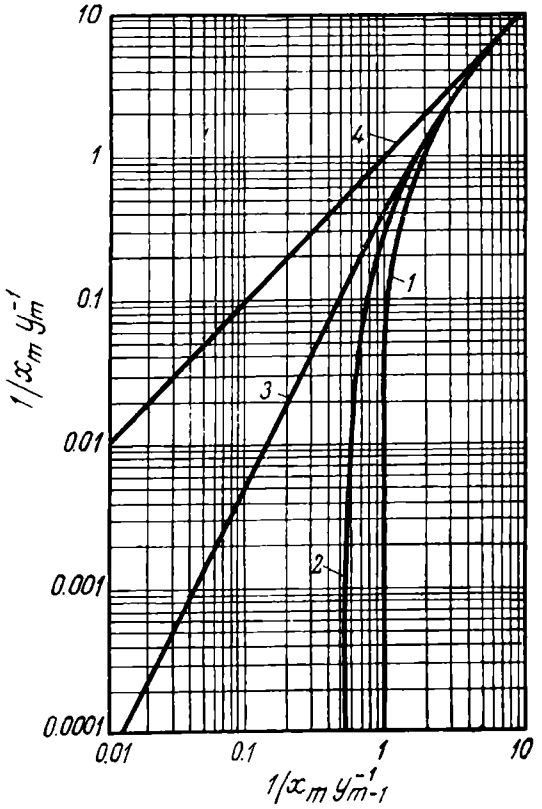


Fig. IV-21. Mixing level in a cascade of reactors at $n = 0$

1 — plugflow or complete micromixing; *2* — laminar segregated flow; *3* — complete segregated mixing; *4* — limit line (diagonal)

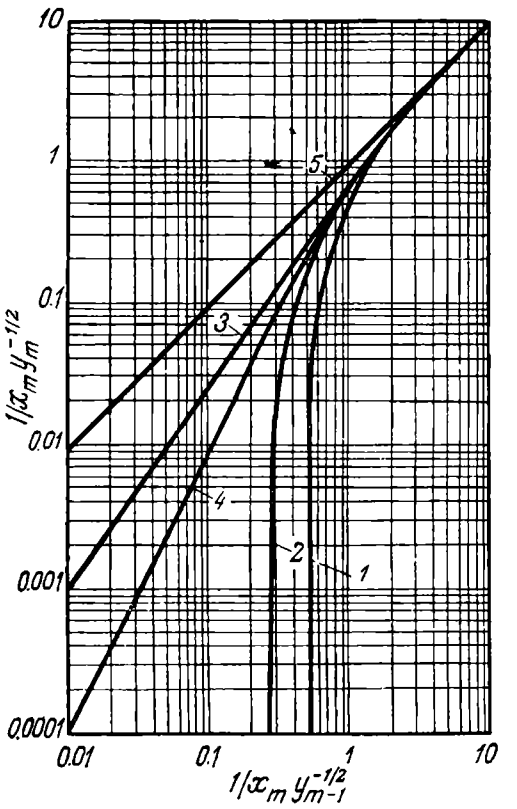


Fig. IV-22. Mixing level in a cascade of reactors at $n = 1/2$

1 — plug flow or batch reactor; *2* — laminar segregated flow; *3* — complete segregated mixing; *4* — complete micromixing; *5* — limit line (diagonal)

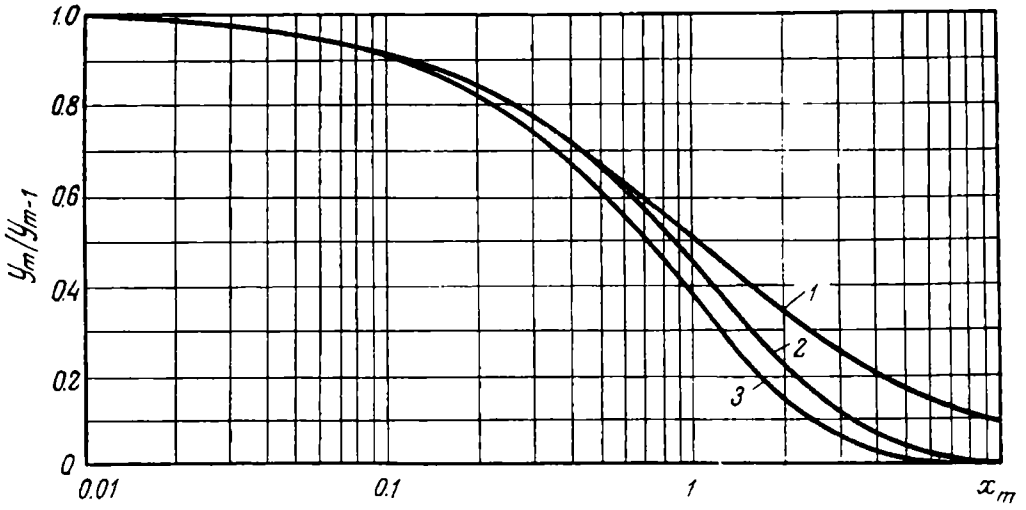


Fig. IV-23. Level of mixing in a cascade of reactors at $n = 1$

1 — complete micro or segregated mixing; *2* — laminar segregated flow; *3* — plug flow or batch reactor

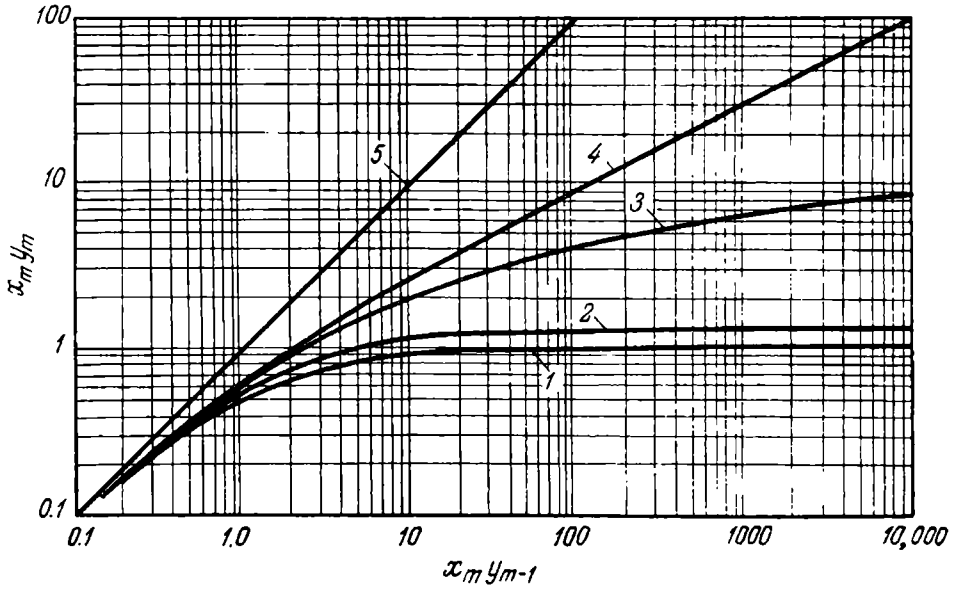


Fig. IV-24. Level of mixing in a cascade of reactors at $n = 2$

1 — plug flow or batch reactor; *2* — laminar segregated flow; *3* — complete segregated mixing; *4* — complete micromixing; *5* — limit line (diagonal)

In cases of non-linear kinetics, use should be made of a correction factor, $f_m = x_m/x_{m-1}$ or $f_m = x_{m-1}/x_m$. In order to obtain a new input value for the mth reactor, the output value of the $(m-1)$th reactor should be multiplied by this factor. For first-order reactions the new value of dimensionless time is found, and new values of the desired fractional conversion will correspond to the ratios y_m/y_{m-1}.

The plots of Figs. IV-21 through IV-24 may also be used to design cascades with side inlets between the reactors, provided the inlets are described by dimensionless relations.

Example IV-4. Consider the esterification of ethyl alcohol by acetic acids at 60°C in the presence of carbon tetrachloride in a cascade of two equal-size tank reactors. The reaction is second order ($n = 2$); the rate constant is $k = 3.768 \times 10^{-2}$ (g mole)$^{-1}$ min^{-1}. The residence time of the reactants in each reactor is $V_R/V_q = 25$ min, and the residence time of the product in the discharge tube is 10 min. Assuming complete microscopic mixing in the reactors and also plug flow in the discharge tube, find the fractional conversion at the exit from the tube into the collector, neglecting the conversion of ethyl alcohol in the connecting tubes between the reactors.

Solution. 1. At the inlet to the first reactor,

$$x_1 y_0 = [k_1 c_{A0}(V_R/V_q)_1]\,(c_{A0}/c_{A0}) = 3.768 \times 10^{-2} \times 1 \times 25 \times (1/1) = 0.944$$

The value at the outlet from the first reactor can be found from the plot of Fig. IV-24: $x_1 y_1 = 0.59$. The same value will exist at the inlet to the second reactor.

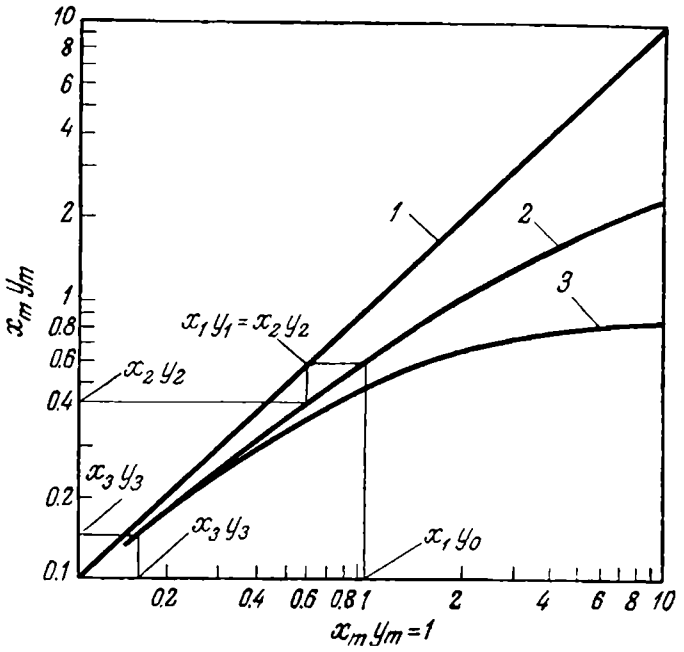


Fig. IV-25. Determination of the number of stages in a cascade of reactors at different levels of mixing

1 — limit curve; *2* — complete micromixing; *3* — plug flow (batch reactor)

In graphical form the above calculations can be represented by constructing the plot of Fig. IV-25, using that of Fig. IV-24 and taking a diagonal as the limit line. Again, the value at the outlet from the second reactor is found from the plot of Fig. IV-24 to be $x_2 y_2 = 0.42$. With a greater number of reactors in a cascade, this step-wise construction is continued until the values $x_3 y_3$, etc. are found (see Fig. IV-25).

2. Since the residence time of the product in the discharge tube differs from that of the reactants in the reactors, we should find the correction

factor

$$f_3 = x_3/x_2 = \frac{k_3 c_{A0}(V_R/V_q)}{k_2 c_{A0}(V_R/V_q)} = 10/25 = 0.4$$

It is assumed that the temperature in the discharge tube is likewise 60°C. Then the value at the inlet to the tube will be

$$x_3 y_2 = (x_2 y_2) f_3 = 0.42 \times 0.4 = 0.168$$

and the outlet value, as found from the plug-flow curve, will be

$$x_3 y_3 = 0.144$$

Hence,

$$y_3 = 0.144/x_3 = 0.144 \div (0.4 \times 0.944)$$

or

$$c_{A3} = 0.144 \div (0.4 \times 0.944 \times 1) = 0.382$$

Thus, the fractional conversion at the tube exit will be

$$(1 - 0.382 \div 1) \times 100 = 61.8\%$$

IV-8. MATHEMATICAL MODELS OF REACTORS WITH HEAT TRANSFER

According to the temperature history of the reaction and the heat transfer involved, all chemical reactors may be classed into isothermal, adiabatic and polytropic.

In an *isothermal* (constant-temperature) *reactor*, as much heat has to be supplied from or rejected into the surroundings as is absorbed or given up by the reaction. Because of the high cost of the equipment needed for this purpose, reactors operating under isothermal conditions are seldom used in large-scale manufacture. Most often, commercial reactors are adiabatic or polytropic types.

In an *adiabatic reactor*, no heat is added or taken away during the process, and that given up by the reaction is wholly utilized within the system to change its enthalpy. The following heat-balance equations apply to adiabatic reactors:

– well-stirred reactors:

$$V_q \rho g c_p (t_f - t_s) = V_q (c_f - c_s)(\pm \Delta H) \qquad \text{(IV-139)}$$

– plug-flow reactors:

$$V_q \rho g c_p \, dt = w_r (\pm \Delta H) \, dV_R \qquad \text{(IV-140)}$$

In a *polytropic reactor*, the heat necessary to sustain the process is added to or taken away from the system. Similarly for a polytropic reactor:

– complete mixing:

$$V_q \rho g c_p (t_f - t_s) = V_q (c_f - c_s)(\pm \Delta H) \pm K_V F (t_f - t_m) \qquad \text{(IV-141)}$$

– plug flow:

$$V_q \rho g c_p \, dt = w_r f (\pm \Delta H) \, dz + K_V F' (t - t_m) \, dz$$
$$= V_q (\pm \Delta H) dc + K_V F' (t - t_m) \, dz \qquad \text{(IV-142)}$$

In the above equations, the notation is as follows:

w_r = reaction rate, kmole m^{-3} h^{-1};
V_q = feed (reaction mixture) flow rate, m^3/h;
ρ = density, kg/m^3;
g = acceleration of gravity, m/s^2;
c_p = heat capacity at constant pressure, J kg^{-1} deg^{-1} (kcal kg^{-1} deg^{-1});
ΔH = heat of reaction, "+" stands for an exothermic reaction, and "–" for an endothermic reaction, J/kmole (kcal/kmole);
t = temperature of the reaction mixture, °C;
t_m = temperature of the heat-transfer medium, °C;
c = reactant concentration, kmole/m^3;
K_V = coefficient of heat transfer from the reaction mixture to the heat-transfer medium, J m^{-2} deg^{-1} (kcal m^{-2} deg^{-1});
F = heat-exchange area, m^2;
F' = heat-exchange area per unit length, m^2/m;
f = cross-sectional area of the stream in the reactor, m^2;
f and s = subscripts standing for "final" and "starting".

In developing mathematical models for adiabatic reactors, it is customary to introduce the *adiabatic change of temperature* given by

$$T_a = (\pm \Delta H)(c_0 - c)/c_p \rho g \qquad \text{(IV-143)}$$

where c_0 and c are the initial and final reactant concentrations.

The maximum adiabatic change of temperature is usually called the *adiabatic temperature*

$$T_a = (\pm \Delta H) c_0 / c_p \rho g \qquad \text{(IV-144)}$$

It will be assumed that in an adiabatic reaction the heat of reaction and the heat capacity of the reaction mixture remain constant. Then a change in temperature T for a given fractional conversion x may be defined[12] as:

$$T = T_0 \pm T_a x \qquad \text{(IV-145)}$$

where T_0 is the initial temperature, T_a is the adiabatic temperature at full conversion, the "+" sign applies to an exothermic reaction and the "–" sign to an endothermic reaction.

Using the Arrhenius equation, we may write

$$k = k_0 \exp(-E/RT) = k_0 \exp[(-E/R)/(T_0 + T_a x)] \qquad \text{(IV-146)}$$

Equation (IV-146) does not contain temperature as a variable. All other conditions being equal, the rate constant is a function of only x, and one can therefore compare various reactions and reactors with relative ease,

provided the parameters E, k, T_a and T_0 or their combinations are properly chosen.

Dispersion model of an adiabatic tubular reactor. To simplify matters, we assume the velocity profile to be flat (a turbulent flow), for which radial gradients may be neglected, and consider a first-order reaction of the type $A \rightarrow R$. Assuming further operation under nonsteady-state conditions, we may write the following equations:

– a mass balance

$$D_L \frac{\partial^2 c}{\partial x^2} - w \frac{\partial c}{\partial x} - kc \exp(-E/RT) = \frac{\partial c}{\partial \tau} \qquad \text{(IV-147)}$$

– an energy (heat) balance

$$\lambda_L \frac{\partial^2 T}{\partial x^2} - w\varrho g c_p \frac{\partial T}{\partial x} + (-\Delta H)\, kc \exp(-E/RT) = \varrho g c_p \frac{\partial T}{\partial \tau} \qquad \text{(IV-148)}$$

The boundary conditions for a tube of a finite length are

$$V_q \varrho g c_p (T_0 - T) = -\lambda_L \frac{\partial T}{\partial x} \qquad (x = 0;\ \tau > 0) \qquad \text{(IV-149)}$$

$$V_q (c_0 - c) = -D_L \frac{\partial c}{\partial x} \qquad (x = 0;\ \tau > 0) \qquad \text{(IV-150)}$$

$$\frac{\partial c}{\partial x} = 0 = \frac{\partial T}{\partial x} \qquad (x = l;\ \tau > 0) \qquad \text{(IV-151)}$$

The initial conditions are:

$$\left.\begin{aligned} T &= T_i(x) \qquad (\tau = 0,\ 0 < x < l) \\ c &= c_i(x) \qquad (\tau = 0,\ 0 < x < l) \end{aligned}\right\} \qquad \text{(IV-152)}$$

In the steady state and under the initial conditions as defined by Eqs. (IV-149) and (IV-150), Eqs. (IV-147) and (IV-148) reduce to the form

$$D_L \frac{\partial^2 c}{\partial x^2} - w \frac{\partial c}{\partial x} - kc \exp(-E/RT) = 0 \qquad \text{(IV-153)}$$

$$\lambda_L \frac{d^2 T}{dx^2} - w c_p \frac{dT}{dx} + (-\Delta H)\, kc \exp(-E/RT) = 0 \qquad \text{(IV-154)}$$

Assuming the same mechanism for heat and mass transport in a turbulent flow, we may write

$$\lambda_L = \varrho g c_p D_L$$

Then the Péclét number will be

$$\mathrm{Pe} = w\varrho g c_p l/\lambda_L = wl/D_L$$

Introducing the adiabatic change in temperature, we get

$$T = T_0 + \frac{(-\Delta H)}{c_p \varrho g}(c_0 + c) \qquad \text{(IV-155)}$$

Then the limiting temperature will be

$$T_{\text{lim}} = T_0 + \frac{(-\Delta H)}{c_p \rho_g} c_0 \qquad \text{(IV-156)}$$

On introducing dimensionless variables, such as

$$y = T/T_0 \qquad z = x/l \qquad g = E/RT_0 \quad \text{and} \quad y_{\text{lim}} = T_{\text{lim}}/T_0$$

Equations (IV-153) and (IV-154) may be reduced to a single expression

$$d^2y/dz^2 + \text{Pe}\, dy/dz + (l^2k/D_L) \exp(-g/y)(y_{\text{lim}} - y) = 0 \qquad \text{(IV-157)}$$

and the boundary conditions may be written as

$$-dy/dz = \text{Pe}(1-y) \qquad z = 0 \qquad \text{(IV-158)}$$

$$dy/dz = 0 \qquad z = 1 \qquad \text{(IV-159)}$$

The equation is solved by integration in a reverse sequence, starting with $z = 1$ and choosing a value for y at $z = 1$, then moving in steps until the value of y_{in} is obtained. If y_{in} be expressed as:

$$y_{in} = \left[-y \frac{1}{\text{Pe}} \frac{dy}{dz}\right] \qquad z = 0$$

the solution is obtained at $y_{in} = 1$. Then, for $z = 1$, y is chosen to lie anywhere between 1 and y_{lim}, and the respective value of y_{in} is found. One or several stable solutions may exist; accordingly there may be one or several stable operating points for the same reactor.

Operating points may be tested for stability by means of Eqs. (IV-147) and (IV-148) which describe nonsteady-state conditions; for a test, all system variables must be specified. Solution is extremely cumbersome and time-consuming and can only be obtained on computers.

Example IV-5.[12] Find the change in temperature and fractional conversion in adiabatic and polytropic plug-flow reactors for the hydrolysis of acetylated castor oil for the manufacture of drying oil at 295 to 340°C according to the scheme:

acetylated castor oil (A) → acetic acid (R) + drying oil (S)

The reaction rate is given by

$$w_r = kc\, \text{CH}_3\text{COOH g cm}^{-3}\text{min}^{-1}$$

The rate constant is given by

$$k = \exp 35.2(-44{,}500/RT)$$

The reaction is endothermic. The heat of reaction is $\Delta H = 62{,}800$ kJ/kmole = 15,000 kcal/kmole CH_3COOH. The initial temperature of the reaction mixture is 340°C. Complete hydrolysis yields 0.156 g of acetic acid per gram of castor oil. The starting charge of castor oil is 500 kg. The reaction is conducted in continuous-flow tubular reactors.

Solution. We assume that the reactor is a plug-flow type. Then, on the basis of Eq. (IV-34), we find the residence time:

$$\tau = c_0 \int_0^x \frac{dx}{w_r} = c_0 \int_0^x \frac{dx}{e^{35.2\left(-\frac{44{,}500}{RT}\right)} c} \qquad (a)$$

Expressing the fractional conversion in terms of $c = c_0(1-x)$, we obtain

$$\tau = \int_0^x \frac{dx}{e^{35.2\left(-\frac{44{,}500}{RT}\right)}(1-x)} \qquad (b)$$

Equation (b) is in three unknowns, τ, T and x. Connection between T and x may be established from a heat balance around the chosen type of reactor.

Adiabatic reactor. According to Eq. (IV-140), a heat balance around this type of reactor is

$$Gc_p\, dT = \Delta H V_m\, dx$$

Putting the average heat capacity of acetylated castor oil at $c_p = 0.6$ and noting that the molecular weight of acetic acid is 60, we get

$$500 \times 0.6\, dT = (-15{,}000)\,(500/60) \times 0.156\, dx$$

whence

$$dT = -65\, dx$$

On substituting the limits of integration and integrating, this equation gives the following connection between T and x:

$$\int_{T_0=340+273}^{T} dt = -65 \int_0^x dx \qquad (c)$$

$$T = 613 - 65x \qquad (d)$$

This relationship is then substituted in Eq. (b). The resultant integral is unlikely to be solved analytically but may readily be solved either graphically or by numerical methods.

Numerical solution. Firstly, we write Eq. (b) in terms of small increments, then we integrate the resultant equation step-wise numerically:

$$\Delta T = \left[\frac{1}{(1-x)e^{35.2\left(-\frac{44{,}500}{RT}\right)}}\right] \Delta x = \left(\frac{1}{R_{av}}\right) \Delta x \qquad (e)$$

Substituting the initial conditions, $T_0 = 613°\text{K}$ and $x_0 = 0$, in Eq. (e), we get

$$1/R_0 = \frac{1}{(1-0)\exp 35.2\left(-\frac{44{,}500}{1.98 \times 613}\right)} = 4.15$$

Choosing $\Delta x = 0.1$ as the initial increment, we obtain from Eq. (*d*):

$$T_1 = 613 - 65 \times 0.1 = 606.5\ ^\circ\text{K}$$

and

$$1/R_1 = \frac{1}{(1-0.1)\exp 35.2\left(-\frac{44{,}500}{1.98 \times 606.5}\right)} = 6.15$$

Thus, for the first increment

$$(1/R)_{av} = (4.15+6.15) \div 2 = 5.15$$

It should be noted that $(1/R)_{av}$ gains in accuracy as the increment size is decreased.

Substituting the found average value in Eq. (*e*), we find the time at the end of the first increment:

$$\Delta\tau_1 = \tau_1 - 0 = 5.15 \times 0.1 - 0 \approx 0.52\ \text{min}$$

Taking $x = 0.2$ as the second increment, from Eq. (*d*) we get

$$T_2 = 613 - 65 \times 0.2 = 600\ ^\circ\text{K}$$

and

$$1/R_2 = \frac{1}{(1-0.2)\exp 35.2\left(-\frac{44{,}500}{1.98 \times 600}\right)}$$

Then $(1/R)_{av}$, $\Delta\tau_2$ and τ_2 are found. The results are tabulated in Table IV-6.

Table IV-6

x	T, °K	τ, min
0	613	0
0.1	606.5	0.52
0.2	600.0	1.40
0.3	503.6	3.00

Graphical integration. A plot of x as a function of T is constructed on the basis of Eq. (*d*) (Fig. IV-26), and the c_0/w_r curve described by the equation

$$c_0/w_r = \frac{1}{(1-x)\exp 35.2(-44{,}500/RT)}$$

is added in the same plot.

For example, at $x = 0.2$ and $T = 600$°K, we have

$$w_r = c_0(1-x)\exp 35.2(-44.500/RT) = 0.8 \exp(-2.2)c_0 = 0.0886c_0$$

$$1/w_r = 11.3/c_0$$

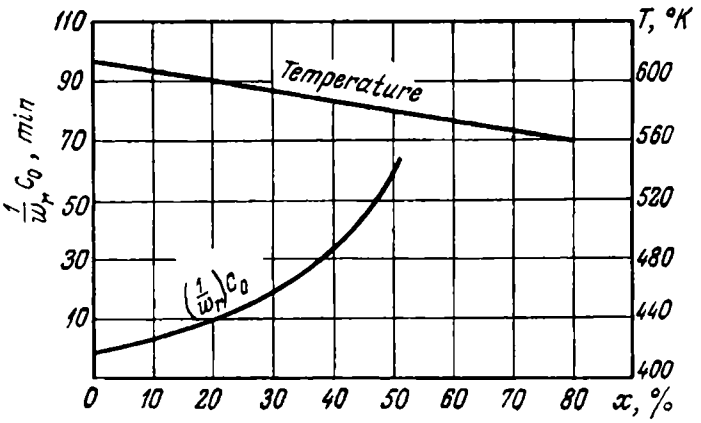


Fig. IV-26. To Example IV-1

From the plot of Fig. IV-26 it also follows that a decrease in temperature during an endothermic reaction in an adiabatic reactor drastically reduces the fractional conversion, and the process comes to a practical standstill at $x = 50\%$. If a higher conversion is sought, heat must be added to the process, that is, a polytropic reactor must be used.

Polytropic reactor. In this case, a heat balance around the reactor is

$$Q\,d\tau + t(-15{,}000)\frac{500}{60}0.156\,dx = 500\times 0.6\,dT$$

On integrating, we get

$$\Delta T = -0.00185Q\,\Delta\tau - 65\,\Delta x \qquad (f)$$

In this case, graphical integration is inapplicable because the connections between T and $1/w_r$, on the one hand, and x are time-dependent. Thus, only numerical integration may be used. Choosing a value of the increment Δx for a specified time interval $\Delta\tau$, we find T_1 at $x_1 = 0 + \Delta x$. Let $Q = -3000$ kcal/min, $\Delta x = 0.1$, and $\Delta\tau = 0.5$ min, which is slightly less than would be chosen for an adiabatic reactor. Then Eq. (f) will give

$$T = 613 + \Delta T_1 = 613 - 65\times 0.1 - 0.00185(-3000)\times 0.5 = 609\ ^\circ\text{K}$$

Now, $(1/R)_{av}$ is found over the range of increments: at $x = 0$

$$R_0 = (1-0)\exp 35.2\left(-\frac{44{,}500}{1.98\times 613}\right); \quad (1/R_0) = 4.15$$

at $x_1 = 0.1$

$$R_1 = (1-0.1)\exp 35.2\left(-\frac{44{,}500}{1.98\times 609.3}\right); \quad (1/R_1) = 5.50$$

and

$$(1/R)_{av} = (4.15+5.50) \div 2 = 4.83$$

Finally, we determine $\Delta\tau$ from Eq. (e):

$$\Delta\tau = 4.83\times 0.1 = 0.48 \text{ min}$$

which is sufficiently close to the assumed value of $\Delta\tau = 0.5$ min.

The above computations can conveniently be carried out on a digital computer. The results are summarized in Table IV-7 which also includes data on an adiabatic reactor.

Table IV-7

x	Adiabatic reactor		Polytropic reactor	
	T, °K	τ, min	T, °K	τ, min
0	613	0	613	0
0.1	605	0.54	608.7	0.48
0.2	600.0	1.43	605.5	1.08
0.3	593.5	2.96	604.0	1.97
0.4	587.0	5.53	603.9	3.10
0.5	580.5	9.85	604.3	4.39

On plotting the above data as shown in Fig. IV-27, we find that a polytropic reactor would have a greater yield.

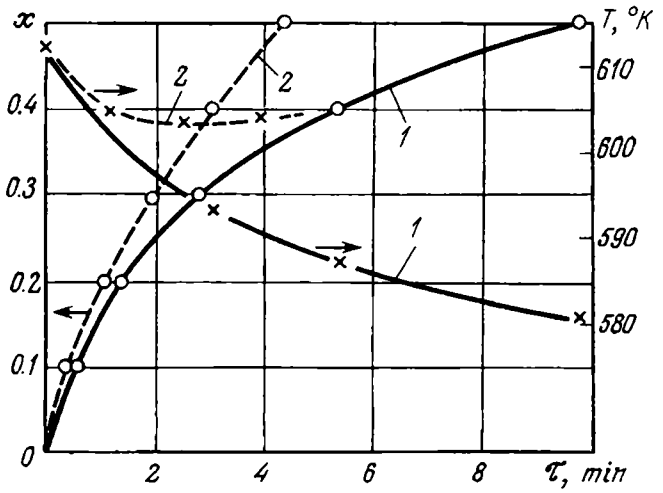


Fig. IV-27. Fractional conversion as a function of time (to Example IV-1)
1 — adiabatic reactor; *2* — polytropic reactor

(A) COMPARISON OF REACTORS UNDER NON-ISOTHERMAL CONDITIONS

Quantitatively, the various reactor types can conveniently be compared on the basis of the slope, $dx/d\tau$, of their x-*versus*-τ curves. These curves can be obtained by differentiating the material balances of the reactors under different conditions of heat transfer and assuming the conditions defined by Eqs. (IV-139) and (IV-140) for adiabatic reactors.

According to Eq. (IV-31), for a plug-flow reactor the slope is given by

$$\mathrm{d}x/\mathrm{d}\tau = c_0^{n-1}k(1-x)^n \qquad \text{(IV-160)}$$

On the basis of Eq. (IV-15) for a well-stirred reactor we have

$$c_0^{n-1}\tau = x/k(1-x)^n \qquad \text{(IV-161)}$$

Differentiating the last equation with respect to the variables x, τ and k gives the following slope:

$$\mathrm{d}x/\mathrm{d}\tau = c_0^{n-1}k(1-x)^n\left[\frac{1-x}{1+(n-1)x-x(1-x)\frac{1}{k}\frac{dk}{dx}}\right] \qquad \text{(IV-162)}$$

From the comparison of Eqs. (IV-160) and (IV-162), [13] it is seen that the slope of the $x-\tau$ curves for a well-stirred reactor differs from that of the same curves for a plug-flow reactor by the factor

$$\left[\frac{1-x}{1+(n-1)x-x(1-x)\frac{1}{k}\frac{dk}{dx}}\right] \qquad \text{(IV-163)}$$

Under isothermal conditions, $dk/dx = 0$, and the factor, (IV-163), reduces to the form

$$\left[\frac{1-x}{1+(n-1)x}\right] \qquad \text{(IV-164)}$$

Since the above factor is always less than unity, the curves of a well-stirred reactor always have a slope smaller than the curves of a plug-flow reactor. Thus, under isothermal conditions a plug-flow reactor will always be more attractive than a well-stirred reactor.

For endothermic reactions, we have

$$dk/dx = \frac{d}{dx}\left[k_0 \exp\left(\frac{-E/R}{T_0 - T_a x}\right)\right] = \frac{-k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1-\frac{T_a}{T_0}x\right)^2} \qquad \text{(IV-165)}$$

Substituting the above expression in Eq. (IV-163) and noting that the factor, (IV-163), is always less than unity, that is, the curve for a well-stirred reactor always has a smaller slope than the curve of a plug-flow reactor, we may write

$$-n\left(1-\frac{T_a}{T_0}x\right)^2 < (1-x)\frac{E}{RT_0}\frac{T_a}{T_0} \qquad \text{(IV-166)}$$

The left-hand side of Eq. (IV-166) is always negative, and the right-hand side is always positive. This is why the factor, (IV-163), is always less than unity. Thus, in the case of endothermic reactions an adiabatic plug-flow reactor will always give a higher conversion per unit volume.

For exothermic reactions we have

$$\mathrm{d}k/\mathrm{d}x = \frac{d}{dx}\left[k_0 \exp\left(\frac{-E/R}{T_0 + T_a x}\right)\right] = \frac{k(E/RT_0)(T_a/T_0)}{\left(1+\frac{T_a}{T_0}x\right)} \qquad \text{(IV-167)}$$

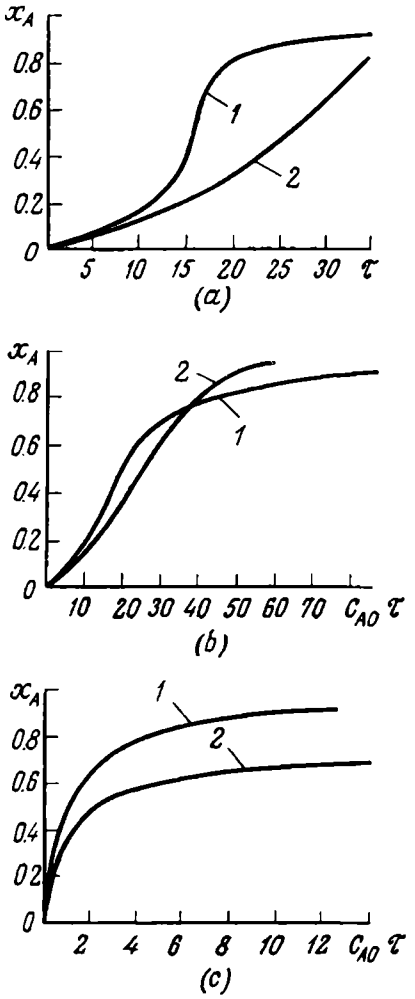


Fig. IV-28. Changes in fractional conversion for different reactions and reactor models (*a*) exothermic first-order reaction; (*b*) exothermic second-order reaction ($M = c_{B0}/c_{A0} = 1.25$); (*c*) endothermic second-order reaction ($M = c_{B0}/c_{A0} = 5$); *1* — complete mixing; *2* — plug flow

In Fig. IV-28, plot (*a*) represents a first-order exothermic reaction, plot (*b*) a second-order exothermic reaction, and plot (*c*) a second-order endothermic reaction at

$$k_{t0} = k_0 \exp(-E/RT_0); \quad k = k_{t0} \exp[4x/(1-0.1x)]$$

$$E/RT_0 = 40; \quad \text{and} \quad T_a/T_0 = 0.1$$

From the plots of Fig. IV-28 and Fig. IV-29 constructed for exothermic reactions on the assumption of microscopic and macroscopic mixing under the same conditions as for the plot of Fig. IV-28, it may be inferred that at relatively low and medium values of x the curves for well-stirred reactors lie somewhat above those for plug-flow reactors. At high values of x, however, the situation is reversed, and the curves of well-stirred reactors have the same slope for both exothermic and endothermic reactions under

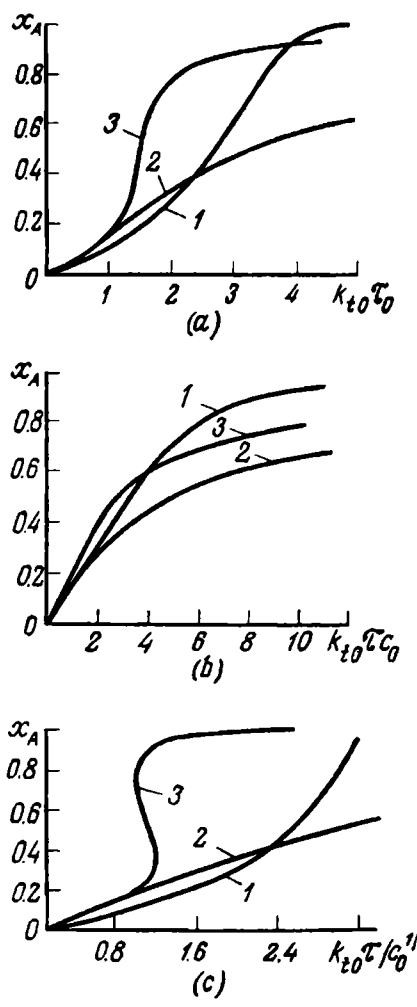


Fig. IV-29. Fractional conversion as a function of mixing level for exothermic reactions in different reactors

(*a*) first-order reaction; (*b*) second-order reaction; (*c*) $^1/_2$-order reaction; *1* — plug flow; *2* — macromixing; *3* — micromixing; $k_{t0} = k_0 \exp(-E/RT_0)$

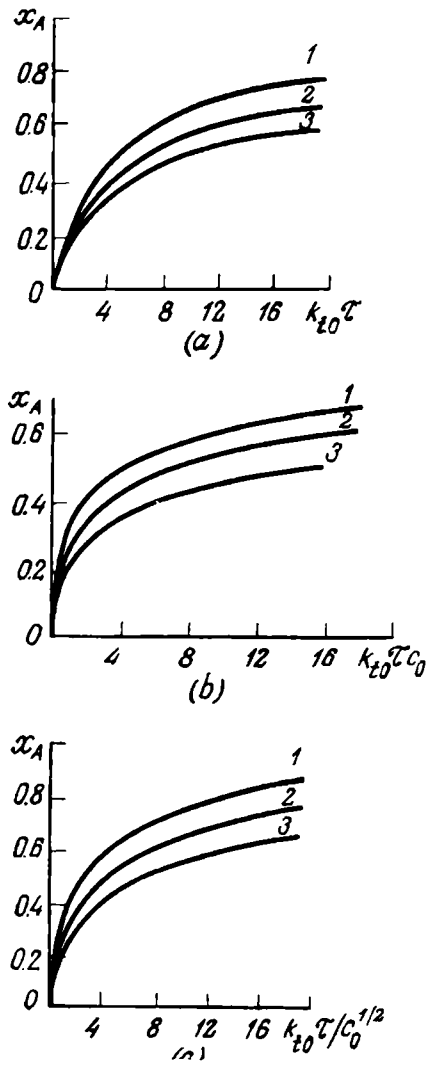


Fig. IV-30. Fractional conversion as a function of mixing level for endothermic reactions in different reactors

(*a*) first-order reaction; (*b*) second-order reaction; (*c*) $^1/_2$-order reaction; *1* — plug flow; *2* — macromixing; *3* — micromixing

isothermal conditions. With endothermic reactions, plug-flow units give a higher conversion than well-stirred reactors do (Fig. IV-30).

The plot of Fig. IV-31 shows the relative residence time, τ_m/τ_b (where τ_m and τ_b are the residence times necessary to attain a desired fractional conversion in a well-stirred and a plug-flow reactor, respectively) as a function of x for endothermic, isothermic and exothermic reactions at the values of k_{t0}, k, E/RT_0 and T_a/T_0 given earlier. As is seen, a well-stirred reactor is more attractive for exothermic reactions than a plug-flow reactor.

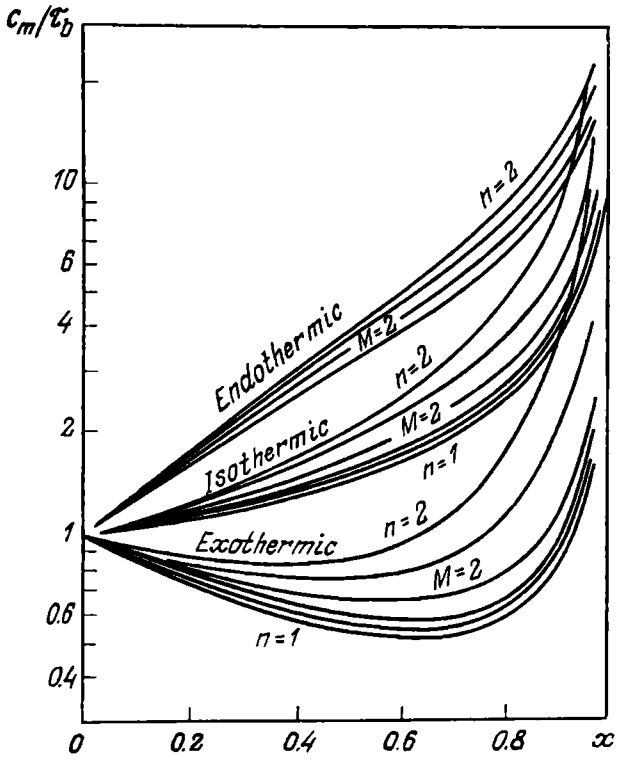


Fig. IV-31. Relative residence time of complete-mixing reactors (τ_m) and plug-flow reactors (τ_b) as a function of fractional conversion for different reactions and different values of $M = c_{B0}/c_{A0}$

Under isothermal conditions and especially with endothermic reactions, the reverse is true, that is, preference should be given to a plug-flow reactor.

From the plots of Fig. IV-29 it is seen that in comparison with a plug-flow reactor the curves of a well-stirred reactor have a greater slope at low values of x, the same slope at some intermediate fractional conversion, and a lower slope at high values of x. Accordingly, on substituting (IV-167) in (IV-163), the factor takes a value greater than unity at low values of x and less than unity at high values of x:

$$\frac{(1-x)\left(1+\frac{T_a}{T_0}x\right)^2}{[1+(n-1)x]\left(1+\frac{T_a}{T_0}x\right)^2 - x(1-x)\frac{E}{RT_0}\frac{T_a}{T_0}} \gtreqless 1 \quad \left.\begin{array}{l}\text{low } x\text{'s}\\ \text{medium } x\text{'s}\\ \text{high } x\text{'s}\end{array}\right. \qquad \text{(IV-168)}$$

or

$$n\left(1+\frac{T_a}{T_0}x\right)^2 \gtreqless (1-x)\frac{E}{RT_0}\frac{T_a}{T_0} \qquad \text{(IV-169)}$$

It is seen from Eq. (IV-169) that at high values of x, that is, with x tending to unity, its right-hand side tends to zero. At a very low fractional conversion

($x \approx 0$), we obtain from Eq. (IV-169):

$$n < \frac{E}{RT_0} \frac{T_a}{T_0} \qquad \text{(IV-170)}$$

Inequality (IV-170) holds for most exothermic systems operating under adiabatic conditions. It should be noted that if this inequality is not obeyed, the reaction rate will decrease with increasing fractional conversion, and a plug-flow reactor will be more attractive than a well-stirred reactor.

These findings may be explained on the basis of the average reaction rates estimated earlier. The rate of endothermic reactions decreases with increasing conversion because the reacting species are depleted, the reaction mixture is diluted by the reaction products, and the temperature in the system goes down. The average reaction rate in a plug-flow reactor (where it is the average of the maximum rate at the inlet and the minimum rate at the exit) is always higher than the average reaction rate in a well-stirred reactor; besides, a high fractional conversion is attained only at high average reaction rates. This is why, under conditions of heat exchange, a plug-flow reactor will be preferable to a well-stirred reactor.

In most exothermic processes, the rate of reaction increases at first with increasing conversion because the temperature in the system rises; at the end, however, the rate decreases with decreasing x because the reacting species are depleted and the reaction mixture is diluted with reaction products. At relatively low conversions, the average reaction rate in a well-stirred reactor is always higher than it is in a plug-flow reactor. On reaching, however, a certain value of x which is slightly above that corresponding to a maximum reaction rate, both types of reactor have identical average reaction rates. Above that value, a plug-flow reactor is more attractive.

The effect of segregation. Changes in the fractional conversion as a function of dimensionless residence time for plug-flow and well-stirred reactors at two levels of mixing in endothermic and exothermic reactions, respectively, are shown in the plots of Figs. IV-29 and IV-30. The profiles have been constructed on the basis of the Arrhenius equation, and the temperature has been eliminated by writing a heat balance around an adiabatic reactor and solving it analytically or graphically at $ER/T_0 = 40$ and $T_a/T_0 = 0.1$.

From a comparison of the segregated state with the molecular mixing level for endothermic reactions (see Fig. IV-30), it is seen that under conditions of segregation a higher fractional conversion is attained in all reaction orders. The difference between this result and that found for isothermal conditions (where the reaction order is an important consideration) stems from the manner in which the reaction rate changes. More specifically, in an endothermic system the reaction rate decreases with increasing conversion (because the reactants are depleted) and with decreasing temperature in the system. In the systems described above, the change in temperature is more than the reaction order can make up for.

A similar comparison for exothermic reactions (see Fig. IV-29) leads to diametrically opposite findings, that is, the fractional conversion is higher

under conditions of molecular mixing. This is because the reaction rate in exothermic systems increases initially with increasing conversion owing to a rise in the system temperature.

(B) HYBRID REACTOR TYPES

Plug flow and complete mixing in series (the $b-m$ model). A typical plot of the fractional conversion as a function of mixing level for exothermic reactions in a plug-flow/well-stirred reactor is shown in Fig. IV-32.[8] The value of x usually changes little at low mixing levels, but it may sometimes

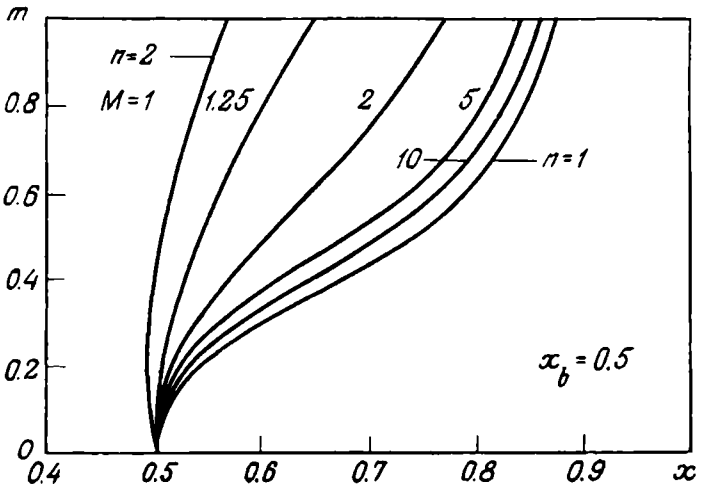


Fig. IV-32. Fractional conversion as a function of mixing level for plug flow — complete mixing models in exothermic reactions of different orders ($M = c_{B0}/c_{A0} = 1$) and of a residence time corresponding to $x_B = 0.5$

experience very sudden changes under certain conditions. With increasing M, the curves for second-order reactions come increasingly closer to those for first-order reactions.

A plot of the relative residence time as a function of mixing level for exothermic reactions in a plug-flow/well-stirred and a straight plug-flow reactor is shown in Fig. IV-33.

Complete mixing and plug flow in series (the $m-b$ model). In order to find the value of x at a specified value of m and residence time τ from the curve for a well-stirred reactor (curve *1* in Fig. IV-34), one should first move as far as point D, then find $\tau_m = m\tau$, and finally determine x_m. When this is done, a line, DB, should be drawn from point D so that it runs parallel to CA, the curve for a plug-flow reactor, until it intersects the axis of abscissae. Then the abscissa of point B will give the total residence time in the system and its ordinate will give the overall fractional conversion for a given endothermic reaction.

A similar construction is done for an exothermic reaction (Fig. IV-35). In any case, the procedure is first to move along the curve for a well-stirred

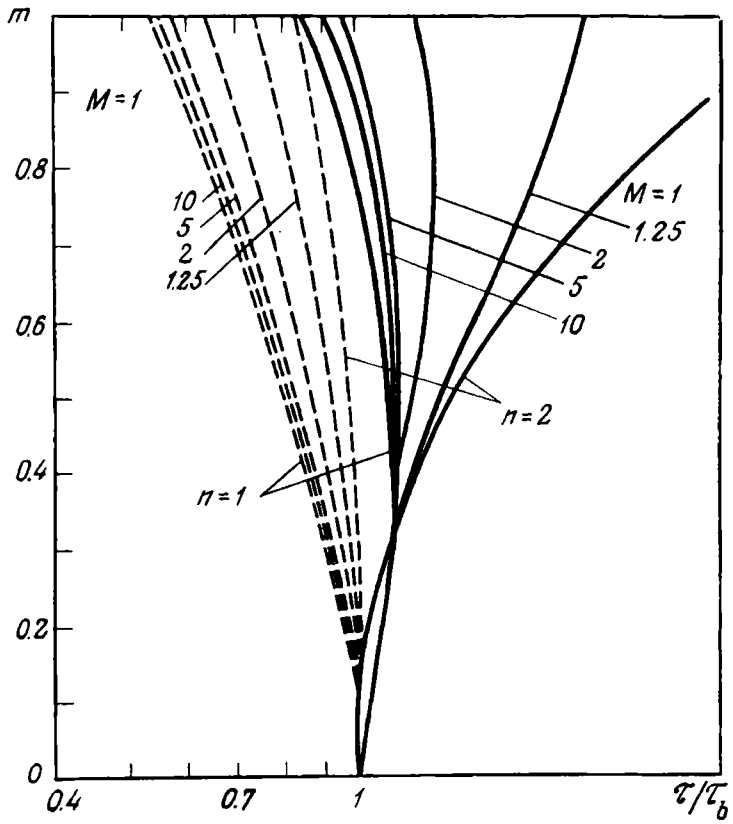


Fig. IV-33. Residence time as a function of mixing level for plug flow — complete mixing and plug-flow reactors in exothermic reactions of different orders, n, and at different values of $M = c_{B0}/c_{A0}$ (the dotted lines, $x = 0.5$; the solid lines, $x = 0.9$)

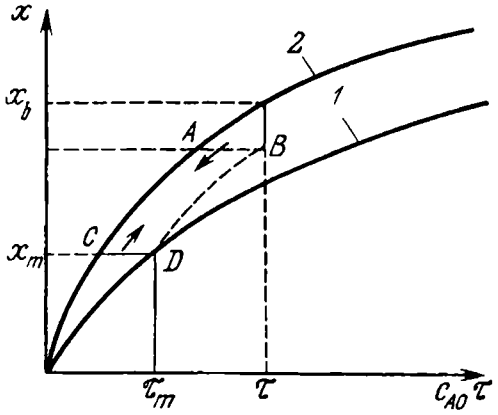


Fig. IV-34. Fractional conversion for a complete mixing — plug flow model carrying out an endothermic reaction

1 — complete mixing; *2* — plug flow

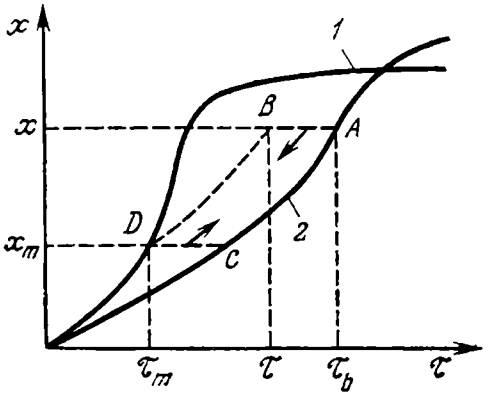


Fig. IV-35. Fractional conversion for a complete mixing — plug flow model carrying out an exothermic reaction

1 — complete mixing; *2* — plug flow

reactor as far as point D representing τ_m, then to draw a straight line parallel to the curve for a plug-flow reactor until it intercepts the value corresponding to τ.

Comparison of the $(b-m)$ and $(m-b)$ models. The two reactor types are compared for exothermic and endothermic reactions and isothermal conditions in Fig. IV-36. While in endothermic reactions and under isothermal conditions, an increase in the level of mixing brings about a decrease in the fractional conversion in both models, the $(b-m)$ model will always show a better performance than the $(m-b)$ model at a given level of mixing. In exothermic reactions, the $(m-b)$ model has a stable effectiveness.

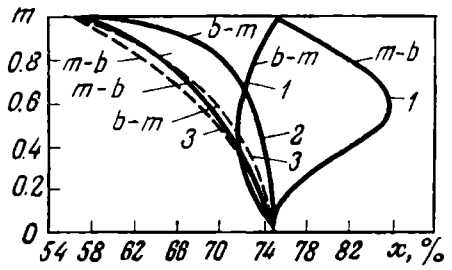


Fig. IV-36. Comparison of hybrid models at different values of m and b for second-order reactions in exothermic processes (line *1*), endothermic processes (line *2*) and under isothermal conditions (line *3*)

The $(m-b)$ model shows a better performance than a straight plug-flow reactor or a straight well-mixed reactor, while the reverse is true of the $(b-m)$ model, because x remains the same at both $m = 0$ and $m = 1$.

To sum up our estimate of an optimum combination of reactor types, we shall consider the construction of a fractional conversion profile.

With exothermic reactions, we plot experimental data on the fractional conversion to obtain a curve for the well-stirred type (curve *1*, Fig. IV-37), as this type gives a faster rate of rise for the final conversion in these conditions.

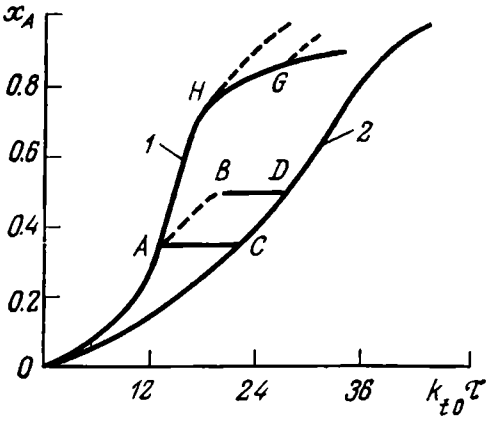


Fig. IV-37. Plot of an optimum hybrid model for exothermic reactions

1 complete mixing; *2* - plug flow

If we plan to construct a combination of a well-stirred and a plug-flow reactor, we shall then plot a second curve (curve *2*, Fig. IV-37) for a plug-flow reactor. Next we choose a point, A, on the curve for the well-stirred reactor where the curve has a maximum slope, and draw from point A a curve, AB, parallel to the curve for the plug-flow reactor between C and D. The line, AB, will then represent the fractional conversion for the combination of the two reactors.

However, this profile does not define an optimum system, because the conditions would be best with a larger well-stirred reactor and a smaller plug-flow reactor. By the same token, if the well-stirred reactor were chosen to operate under conditions defined by point G, the conditions in the system would be best with a smaller well-stirred reactor. It is seen that an optimum

combination of reactors will be at point H (where the two curves have the same slope).

To sum up, a plug-flow reactor is always a better choice under isothermal conditions and for endothermic reactions, while a combination of a well-stirred and a plug-flow reactor will be more attractive for exothermic reactions.

Example IV-6. Find the value of x for a $(b-m)$ reactor. Given: an exothermic process, a first-order reaction, process time is $\tau = 34$ s; the fraction of the well-stirred region is $m = 0.3$.

Solution. At $m = 0.3$, the time $\tau_b = 0.7 \times 34 = 23.8$ s. On constructing a plot similar to that in Fig. IV-35 at a residence time of 23.8 s, we get $x_b = 0.39$.

For the $(b-m)$ model we find $x = 0.79$ by trial and error, and from the curve for the well-stirred reactor find $\tau = 20.1$. On multiplying this value by $(1-x_b)/x)$, we get:

$$\tau_m = 20.1\left(1-\frac{0.39}{0.79}\right) = 10.2 \text{ s}$$

The same value will be found from

$$\tau_m = m\tau = 0.3\,(23.8+10.2) = 10.2 \text{ s}$$

At $\tau = 34$ s, a plug-flow reactor will give $x = 0.75$, while the $(b-m)$ model will give $x = 0.79$ at $m = 0.3$.

Example IV-7. Find the ratio of the residence time, τ, in a $(b-m)$ reactor to the residence time, τ_b, in a plug-flow reactor and the fraction, m, of the corresponding complete-mixing region at $x = 0.5$. The reaction is second-order, exothermic; $M = c_{B0}/c_{A0} = 1.25$, and the residence time in the plug-flow region is such that $c_{A0}\tau_b' = 10$.

Solution. For $c_{A0}\tau_b' = 10$, from the plug-flow curve we get $x_b' = 0.145$. At $x = 0.5$, from the complete-mixing curve we find $c_{A0}\tau_m = 19.9$. Multiplying this value by $(1-x_b'/x)$ gives

$$c_{A0}\tau_m' = 19.9\left(1-\frac{0.145}{0.50}\right) = 14.1$$

The overall value is

$$c_{A0}\tau_m = 14.1+10 = 24.1$$

Therefore,

$$m = \tau_m'/\tau = 14.1 \div 24.1 = 0.58$$

At $x = 0.50$, from the plug-flow curve (see Fig. IV-34) we get

$$c_{A0}\tau_b = 26.7$$

and at $m = 0.58$

$$\tau/\tau_b = 24.1 \div 26.7 = 0.90$$

Example IV-8. Find the fractional conversion for an $(m-b)$ reactor. The reaction is second-order (endothermic); $M = c_{B0}/c_{A0} = 5$, $c_{A0}\tau = 12$, and $m = 0.7$.

Solution. From the complete-mixing curve we find that at $x'_m = 0.67$ the conditions existing at point D are $c_{A0}\tau'_m = 0.7 \times 12 = 8.4$. Then from the plot it is found that the ordinate of point B gives an overall fractional conversion of $x = 0.81$. Thus, $x = 0.9$ can be obtained only in a plug-flow reactor at $c_{A0}\tau = 12$.

Example IV-9. Find the relative residence time and the size m of the well-stirred region in an $(m-b)$ reactor at $x = 0.9$. Given: a second-order (exothermic) reaction, $M = c_{B0}/c_{A0} = 1.25$, and $c_{A0}\tau'_m = 20$.

Solution. On the complete-mixing curve, $c_{A0}\tau'_m = 20$ is found to exist at point D. We extend the straight-line segment, DB, parallel to the segment, CA, of the plug-flow curve as far as $x = 0.9$. The abscissa of point B gives $c_{A0}\tau = 40.8$. Then, $m = 20/40.8 = 0.49$. At $x = 0.9$, from the plug-flow curve, we obtain $c_{A0}\tau_b = 47.5$. At $m = 0.49$, the ratio $M = 40.8/47.5 = 0.86$.

(C) PLUG-FLOW REACTORS WITH BYPASSING

According to Eq. (IV-31), for a single plug-flow reactor and a first-order exothermic reaction we have

$$dx/d\tau = k(1-x) \tag{IV-171}$$

At an initial temperature T_0, we may write

$$k_{t0} = k_0 \exp(-E/RT_0) \tag{IV-172}$$

Using Eq. (IV-146), from a heat balance around an adiabatic reactor we get

$$k_{t0}\tau = k_{t0}\frac{V_R}{V_q} = \int_{x_0}^{x} \exp\left(-\frac{\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x}{1+\frac{T_a}{T_0}x}\right)\frac{dx}{1-x} = \int_{x_0}^{x}\Phi(x)\frac{dx}{1-x} \tag{IV-173}$$

The above integral reduces to a sum of tabulated exponential integrals.

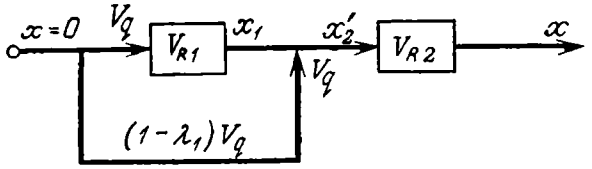


Fig. IV-38. Two plug-flow reactors with a bypass

The diagram of Fig. IV-38 shows two plug-flow reactors with a fraction, $1-\lambda_1$, of the feed stream bypassed. A material balance around the point where the streams are mixed is

$$x'_2 = x_1\lambda_1 \tag{IV-174}$$

The individual reactors are described by equations of the form

$$k_{10}\frac{V_{R1}}{V_q} = \lambda_1 \int_0^{x_1} \Phi(x)\frac{dx}{1-x} \tag{IV-175}$$

and

$$k_{10}\frac{V_{R2}}{V_q} = \int_0^{x} \Phi(x)\frac{dx}{1-x} = \int_{x_1\lambda_1}^{x} \Phi(x)\frac{dx}{1-x} \tag{IV-176}$$

The values of x_1 and λ_1 which minimize the system hold-up can be found by equating the partial derivatives to zero:

$$\partial(V_{R1}+V_{R2})/\partial x_1 = \partial(V_{R1}+V_{R2})/\partial\lambda_1 = 0 \tag{IV-177}$$

After differentiation and transformation, we get

$$\int_0^{x_1} \Phi(x)\frac{dx}{1-x} = \frac{x_1}{1-x_1}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_1}{1-\frac{T_a}{T_0}x_1}\right) \tag{IV-178}$$

$$\int_0^{x_1} \Phi(x)\frac{dx}{1-x} = \frac{x_1}{1-x_1\lambda_1}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_1\lambda_1}{1-\frac{T_a}{T_0}x\lambda_1}\right) \tag{IV-179}$$

Equations (IV-178) and (IV-179) can be solved for x_1 and λ_1 by trial and error. The convergence is attained rapidly. Once the optimum values of x_1 and λ_1 are found, the reactor hold-ups can readily by determined from Eqs. (IV-175) and (IV-176).

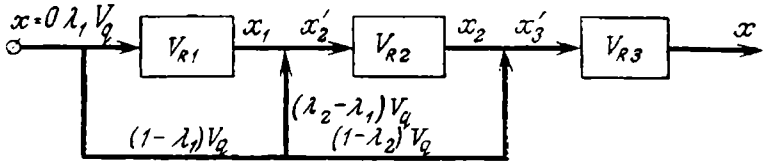


Fig. IV-39. Three plug-flow reactors with a bypass

For three reactors with bypassing (Fig. IV-39), we have:
material balances around the points of mixing:

$$x_2^1 = x_1\lambda_1/\lambda_2 \tag{IV-180}$$

$$x_3^1 = x_2\lambda_2 \tag{IV-181}$$

reactor hold-ups:

$$k_{l0}\frac{V_{R1}}{V_q} = \lambda_1 \int_0^{x_1} \Phi(x)\frac{dx}{1-x} \tag{IV-182}$$

$$k_{l0}\frac{V_{R2}}{V_q} = \lambda_2 \int_{x_2'}^{x_2} \Phi(x)\frac{dx}{1-x} = \lambda_2 \int_{\frac{x_1\lambda_1}{\lambda_2}}^{x_2} \Phi(x)\frac{dx}{1-x} \tag{IV-183}$$

$$k_{l0}\frac{V_{R2}}{V_q} = \int_{x_3'}^{x} \Phi(x)\frac{dx}{1-x} = \int_{x\lambda_2}^{x} \Phi(x)\frac{dx}{1-x} \tag{IV-184}$$

Putting

$$\frac{\partial(V_{R1}+V_{R2}+V_{R3})}{\partial\lambda_1} = \frac{\partial V_t}{\partial\lambda_1} = \frac{\partial V_t}{\partial x_1} = \frac{\partial V_t}{\partial\lambda_2} = \frac{\partial V_t}{\partial x_2} = 0 \tag{IV-185}$$

we get

$$\int_0^{x_1} \Phi(x)\frac{dx}{1-x} = \frac{x_1}{1-x_1}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_1}{1+\frac{T_a}{T_0}x_1}\right) \tag{IV-186}$$

$$\int_0^{x_2} \Phi(x)\frac{dx}{1-x} = \frac{x_1}{1-x_1\frac{\lambda_1}{\lambda_2}}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_1\frac{\lambda_1}{\lambda_2}}{1+\frac{T_a}{T_0}x_1\frac{\lambda_1}{\lambda_2}}\right) \tag{IV-187}$$

$$\int_{x_1\frac{\lambda_1}{\lambda_2}}^{x_2} \Phi(x)\frac{dx}{1-x} + \frac{x_1\frac{\lambda_1}{\lambda_2}}{1-x_1\frac{\lambda_1}{\lambda_2}}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_1\frac{\lambda_1}{\lambda_2}}{1+\frac{T_a}{T_0}x_1\frac{\lambda_1}{\lambda_2}}\right) = \frac{x_2}{1-x_2}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_1\frac{\lambda_1}{\lambda_2}}{1+\frac{T_a}{T_0}x_1\frac{\lambda_1}{\lambda_2}}\right)$$

$$= \frac{x_2}{1-x_2}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_2}{1+\frac{T_a}{T_0}x_2}\right) \tag{IV-188}$$

$$\frac{1}{1-x_2}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_2}{1+\frac{T_a}{T_0}x_2}\right) = \frac{1}{1-x\lambda_2}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_2\lambda_2}{1+\frac{T_a}{T_0}x_2\lambda_2}\right) \tag{IV-189}$$

Equation (IV-186) is fully identical with Eq. (IV-178). Therefore, the fractional conversion downstream from the first reactor in a cascade of three reactors is the same as in a cascade of two reactors. Similarly, Eqs. (IV-179) and (IV-187) give the same ratio λ_1/λ_2 for a cascade of three reactors as for a cascade of two reactors. Eq. (IV-188) can be solved for x_2 by trial and error, because x_1 and λ_1/λ_2 are unknown. Then Eq. (IV-189) is solved in a

similar way for λ_2. The reactor hold-ups are found from Eqs. (IV-182) through (IV-184).

With four reactors in a cascade, we only need to add an appropriate equation for the fourth reactor to our analysis. The fractional conversion at the exit from the first two reactors will be the same as in a cascade of three reactors, and the ratio λ_1/λ_2 will be constant. From a comparison of the equations it is seen that λ_2 in a three-stage system should be equal to λ_2/λ_3 in a four-stage system. To find the values of x_3 and λ_3, the following equations need be solved by trial and error:

$$\int_{x_2\frac{\lambda_2}{\lambda_3}}^{x_3} \Phi(x)\frac{dx}{1-x} + \frac{x_2\frac{\lambda_2}{\lambda_3}}{1-x_2\frac{\lambda_2}{\lambda_3}} \exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_2\frac{\lambda_2}{\lambda_3}}{1-\frac{T_a}{T_0}x_2\frac{\lambda_2}{\lambda_3}}\right)$$

$$= \frac{x_3}{1-x_3}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_3}{1+\frac{T_a}{T_0}x_3}\right) \qquad \text{(IV-190)}$$

$$\frac{1}{1-x_3}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_3}{1+\frac{T_a}{T_0}x_3}\right) = \frac{1}{1-x_3\lambda_3}\exp\left(\frac{-\frac{E}{RT_0}\cdot\frac{T_a}{T_0}x_3\lambda_3}{1+\frac{T_a}{T_0}x_3\lambda_3}\right) \qquad \text{(IV-191)}$$

IV-9. THERMAL STABILITY OF CHEMICAL REACTORS

With exothermic reactions, a crucial problem in the optimization and control of chemical reactors is that of thermal stability.

For the first time, the stability of a system was defined by A. Lyapunov as follows: „A system is stable if, upon application of a disturbance, it returns to its original state when the disturbance is removed".[14]

As regards chemical reactors with exothermic reactions, various disturbances (changes in the amount of reacting components, impairment of heat abstraction, fluctuations in the feed composition, etc.) may force a process to move away from a steady state so far that it will not be able to return to its original state of its own accord. This is why it is vitally important to evaluate the steady-state (operating-point) stability of chemical reactors. We shall take up the problem, using polytropic reactors.

General. An estimate of the stability of a reactor can be derived from its nonsteady-state (dynamic) equations:

$$V_R\frac{dc_A}{d\tau} = V_q/(c_{A0}-c_A) - V_R k_0(T)c_A^n \qquad \text{(IV-192)}$$

$$\rho g V_q c_p\frac{dT}{d\tau} = V_q\rho g c_p(T_0-T) - K_V F(T-T_x) + V_R k_0(T)c_A^n(-\Delta H) \qquad \text{(IV-193)}$$

linearized in the vicinity of the operating point under study.

On linearizing Eqs. (IV-192) and (IV-193) for first-order reactions ($n = 1$), we get

$$\left.\begin{aligned} \frac{d\Delta c_A}{d\tau} &= -\left[\frac{1}{\tau}+k_0(T_s)\right]\Delta c_A - \frac{E}{RT^2}k_0(T_s)_2 c_{As}\Delta T \\ \frac{d\Delta T_A}{d\tau} &= \frac{\Delta H}{c_p\varrho g}k_0(T_s)\,\Delta c_A \\ &- \left[\frac{1}{\tau}+\frac{K_V}{V_q\varrho g c_p}-\frac{\Delta H}{\varrho g c_p}\,\frac{E}{RT^2}k_0(T_s)c_{As}\right]\Delta T \end{aligned}\right\} \quad \text{(IV-194)}$$

where Δc_A is the deviation of the concentration from the value, c_{As}, at the operating point under study and ΔT_A is the deviation of the temperature from the value, T_s, existing at that point.

The values of c_A and T_s can be found by solving the equations describing the operating conditions in a steady state:

$$\begin{aligned} V_q(c_{A0}-c_A)-V_R k_0(T)c_A &= 0 \\ V_q\varrho g c_p(T_0-T)-K_V F(T-T_m)+V_R k_0(T)c_A\Delta H &= 0 \end{aligned} \quad \text{(IV-195)}$$

Equations (IV-194) may be re-written as

$$\left.\begin{aligned} d\Delta c_A/\Delta\tau &= \alpha_{11}\Delta c_A+\alpha_{12}\Delta T \\ d\Delta T_A/d\tau &= \alpha_{21}\Delta c_A+\alpha_{22}\Delta T \end{aligned}\right\} \quad \text{(IV-196)}$$

where α_{ik} represents the respective coefficients in Eqs. (IV-194).

The system described by Eqs. (IV-196) and, as a consequence, the operating conditions will be stable, if the roots λ_0 of the characteristic equation of the system, Eq. (IV-196)

$$\begin{aligned} \begin{vmatrix} \alpha_{11}-\lambda & \alpha_{12} \\ \alpha_{21} & \alpha_{22}-\lambda \end{vmatrix} &= \lambda^2-(\alpha_{11}+\alpha_{22})\lambda+\alpha_{11}\alpha_{22} \\ &-\alpha_{21}\alpha_{12} = 0 \end{aligned} \quad \text{(IV-197)}$$

are negative real numbers or, if they are complex numbers, have negative real parts.

This will be so if the following conditions are satisfied:

$$-(\alpha_{11}+\alpha_{22}) > 0 \quad \text{(IV-198)}$$

$$\alpha_{11}\alpha_{22}-\alpha_{12}\alpha_{21} > 0 \quad \text{(IV-199)}$$

which, on substituting the expressions for α_{ik} from Eqs. (IV-194), have the form

$$\frac{2}{\tau}+\frac{K_T F}{V_q\varrho g c_p}+k_0(T_s)-\frac{(\Delta H)E}{\varrho g c_p RT^2}k_0(T_s)c_A > 0 \quad \text{(IV-200)}$$

$$[1+k_0(T_s)\tau]\left(1+\frac{K_V F}{V_q\varrho g c_p}\right)-\frac{(\Delta H)E}{\varrho g c_p RT^2}k_0(T_s)c_A > 0 \quad \text{(IV-201)}$$

The physical significance of Eq. (IV-201) may be grasped, if it is re-written as

$$V_q\rho g c_p + K_V F > V_R(-\Delta H)(E/RT^2)\frac{k_0(T_s)c_0}{\left[1+\frac{V_R}{V_q}k_0(T_s)\right]^2} \qquad \text{(IV-202)}$$

The left-hand side of Eq. (IV-202) is the temperature derivative of the heat removed from the reactor, which is given by

$$Q_{rem} = V_q\rho g c_p T + K_V F(T - T_m)$$

whence

$$dQ_{rem}/dT = V_q\rho g c_p + K_V F$$

It may be shown that the right-hand side of inequality (IV-202) is a derivative of the heat generated in the reactor, because

$$Q_{gen} = V_R(-\Delta H)\frac{k_0(T_s)c_{A0}}{1+\frac{V_R}{V_q}k_0(T_s)} + V_q T_0$$

and, therefore,

$$dQ_{gen}/dT = V_R(-\Delta H)(E/RT^2)\frac{k_0(T_s)c_{A0}}{\left[1+\frac{V_R}{V_q}k_0(T_s)\right]^2}$$

Thus, (IV-201) or (IV-202) reduces to the following

$$dQ_{rem}/dT > dQ_{gen}/dT \qquad \text{(IV-203)}$$

that is, the Q-*vs*-T curve should have a greater slope for the heat removed than for the heat generated.

In the general case, for the operating conditions of a reactor to have a good measure of stability, it is essential to satisfy the conditions defined by (IV-200) and (IV-201). As often as not, however, whether a reactor is operating under conditions of stability may be decided on the basis of (IV-200) or (IV-201). By combining (IV-200) and (IV-201), it may be shown that if the inequality

$$\tau < \frac{V_q\rho g c_p}{K_T F}\frac{1-x}{x} \qquad \text{(IV-204)}$$

is satisfied, then (IV-202) and, as a consequence, (IV-203) is the necessary and sufficient condition for the stability of a reactor's operating point. If inequality (IV-204) is not satisfied, the necessary and sufficient condition for the stability of the operating point is given by (IV-200).

The condition defined by (IV-203) may be graphically interpreted by use of an S-shaped diagram which is a temperature profile for a well-stirred reactor in which the temperature rises rapidly at low values of fractional conversion and slows down as rapidly at high values of x. In other words, the rate of heat generation is high at first and much lower when a high fractional conversion has been attained.

The amount of heat removed under adiabatic conditions is wholly determined by the difference in heat content between the streams at the inlet to and the exit from a reactor. This may be represented by a straight line crossing the axis of abscissae at point T_0 (the inlet temperature). Under polytropic conditions, the heat removal line runs at a lower temperature determined by that of the heat-transfer medium.

From the plot of Fig. IV-40 it is seen that the heat generation and heat removal lines may have several intersections, that is, there may exist several points at which the amount of heat removed is equal to that supplied, or, which is the same, there may be several steady operating points (or operating conditions). Generally, the location of intersections depends on the choice of process variables (inlet temperature, fractional conversion, and residence time) and reaction kinetics (see Figs. IV-29 and IV-30).

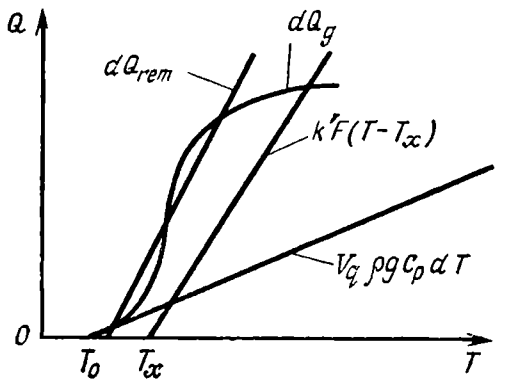


Fig. IV-40. Explaining reactor stability conditions $d\theta_{rem}$ – heat removed; $d\theta_g$ – heat generated

If the heat removal line runs above the heat input line, the area above the intersections defines the region where the reactor will operate under conditions of stability. If, however, the heat removal line runs below the heat input line, the reactor will operate under conditions of instability.

Well-stirred reactor.[15] As follows from the foregoing, the amount of heat removed from the system in a polytropic reactor is given by

$$V_q \rho g c_p (T_f - T_0) + K_V F_V V_R (T_f - T_m) \qquad \text{(IV-205)}$$

where F_V is the heat-exchange area, m^2/m^3, T_f is the final temperature and T_m is the temperature of the heat-transfer medium.

On introducing the adiabatic temperature, we can express the amount of heat removed in dimensionless form as follows:

$$Q'_{rem} = \frac{1 + K_V (F_V \tau_r / \rho g c_p)}{T_a} (T_f - T'_0) \qquad \text{(IV-206)}$$

where T'_0 is the apparent temperature of the reaction mixture at the inlet to the reactor:

$$\frac{T'_0 - T_0}{T_m - T_0} = \frac{K_V F_V \tau_r / \rho g c_p}{1 + (K_V F_V \tau_r / \rho g c_p)} \qquad \text{(IV-207)}$$

It follows from Eqs. (IV-206) and (IV-207) that the heat removal and inlet temperature depend on the residence time τ_r or the feed rate.

Consider simultaneous reactions of the type

$$A \xrightarrow{k_1} R, \quad w_{rR} = k_1 c_A; \quad A \xrightarrow{k_2} S, \quad w_{rS} = k_2 c_A$$

and consecutive reactions of the type

$$A \rightarrow R, \quad w_{rA} = k_1 c_A, \quad w_{rR} = k_1 c_A - k_2 c_R$$
$$R \rightarrow S, \quad w_r = k_2 c_R$$

We choose R to be the wanted product and S an unwanted product. For a simultaneous reaction, the amount of heat generated is given by

$$-[\Delta H_1 k_1 + \Delta H_2 k_2]\, c_A V_R \tag{IV-208}$$

where c_A is the concentration of reactant A in a well-stirred reactor given (see Table IV-3) by

$$c_A = \frac{c_{A0}}{1-(k_1+k_2)\tau_r} \tag{IV-209}$$

To express the heat generated in dimensionless form, we divide the heat actually given up into that ultimately available as expressed by

$$\left.\begin{aligned} -\Delta H_2 c_{A0} V_q \quad &\text{at} \quad \Delta H_1 < \Delta H_2 \\ -\Delta H_1 c_{A0} V_q \quad &\text{at} \quad \Delta H_1 > \Delta H_2 \end{aligned}\right\} \tag{IV-210}$$

Then, on introducing $H = \Delta H_2/\Delta H_1$, we get ($a$) at $H > 1$,

$$Q_r' = \frac{(k_1+k_2 H)\tau_r}{[1+(k_1+k_2)\tau_r]H} \tag{IV-211}$$

(b) at $H < 1$,

$$Q_r' = \frac{(k_1+k_2 H)\tau_r}{1+(k_1+k_2)\tau_r} \tag{IV-212}$$

where Q_r' is the heat generated by the reaction.

For consecutive reactions, the heat generated is given by

$$-V_R[\Delta H_1 k_1 c_A + \Delta H_2 k_2 c_R] \tag{IV-213}$$

For a steady state, we have

$$c_A = c_{A0}/(1+k_1\tau_r) \quad \text{and} \quad c_R = k_1\tau_r c_{A0}/(1+k_1\tau_r)\,(1+k_2\tau_r)$$

Then the heat ultimately available will be

$$-(\Delta H_1 + \Delta H_2) c_{A0} V_q \tag{IV-214}$$

whence

$$Q_r' = \frac{k_1\tau_r[1+(1+H)k_2\tau_r]}{(1+k_1\tau_r)\,(1+k_2\tau_r)\,(1+H)} \tag{IV-215}$$

For a consecutive reaction:

$$T_a = \frac{-\Delta H_1 c_{A0}(1+H)}{\rho g c_p}$$

To compare the manner in which the two types of reaction proceed, we introduce the temperature, T_R, at which the rate constant, k_1, of the desired

reaction and the rate constant, k_2, of the unwanted reaction become equal to k_R

$$k_1 \exp(E_1/RT_R) = k_2 \exp(-E_2/RT_R) = k_R \qquad \text{(IV-216)}$$

$$T_R = \frac{E_1(b-1)}{R \ln(k_2/k_1)} \qquad k_R = (k_1/k_2)\, 1/(b-1) \qquad \text{(IV-217)}$$

where $b = E_2/E_1$.

The ratio of activation energies, b, is a measure of change in selectivity with temperature, selectivity being defined as the ratio $c_R/(c_R+c_S)$. The more b differs from unity, the greater the change in the selectivity with temperature. At $b > 1$, the selectivity increases with falling temperature; at $b < 1$, the selectivity increases with rising temperature.

Now we shall introduce dimensionless terms. Let $K = k_1/k_R$ be the rate constant of the first reaction; $K_b = k_2/k_R$ be the rate constant of the second reaction; $T = T_f/T_R$ the reactor temperature, and $\theta = k_R V_R/V_q$ the residence time.

If $b > 1$, the reactor is operating at a temperature level $T < 1$; if $b < 1$, the reactor is operating at a temperature level $T > 1$ and a high selectivity. With the values of b, RT_R/E_1, H and τ_r specified in advance, the following dimensionless equation may be used to determine Q'_{rem} and Q'_r:

$$Q'_{rem} = \frac{1+(K_V F_V \theta/\rho g c_q k_R)}{T_a}(T_f - T'_0) \qquad \text{(IV-218)}$$

For simultaneous reactions we have:

(*a*) at $H > 1$

$$T_a = -c_{A0} H_1 H/\rho g c_p T_R \qquad \text{(IV-219)}$$

$$Q'_r = \frac{(K+K_b H)\theta}{[1+(K+K_b)\theta]H} \qquad \text{(IV-220)}$$

(*b*) at $H < 1$

$$T_a = -c_{A0}\, \Delta H_1/\rho g c_p T_R \qquad \text{(IV-221)}$$

$$Q'_r = \frac{(K+K_b H)\theta}{1+(K+K_b)\theta} \qquad \text{(IV-222)}$$

For consecutive reactions we get

$$T_a = -c_{A0}\, \Delta H_1(1+H)/\rho g c_p T_R \qquad \text{(IV-223)}$$

$$Q'_r = \frac{K\theta[1+(1+H)K_b\theta]}{(1+K\theta)(1+K_b)(1+H)} \qquad \text{(IV-224)}$$

From the above equations, the dimensionless reactor temperature may be defined as

$$T = \frac{1}{1-(RT_R/E_1)\ln K} = \frac{1}{1-[(b-1)/\ln(k_2/k_2)]\ln K} \qquad \text{(IV-225)}$$

In generalized form, plots of Q'_r and $c_R/(c_R+c_S)$ as functions of dimensionless reactor temperature T and dimensionless residence time, θ, are given

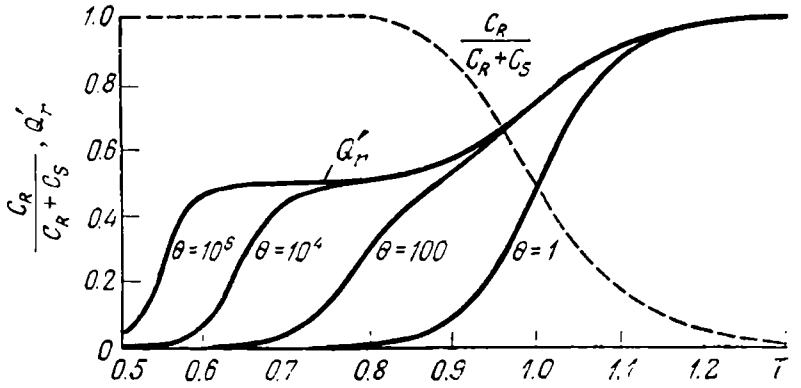


Fig. IV-41. Heat generation and yield in simultaneous reactions as a function of residence time and reactor temperature ($H = 2$, $b = 2$, $E_1/RT_R = 16.7$)

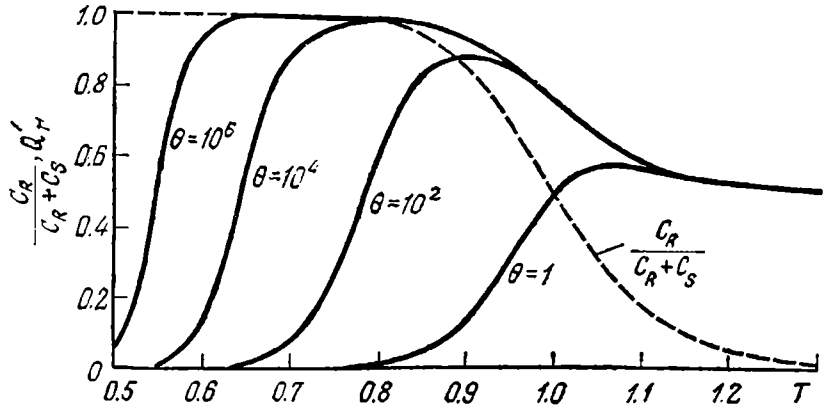


Fig. IV-42. Heat generation and yield in simultaneous reactions as a function of residence time and reactor temperature ($H = 0.5$, $b = 2$, $E_1/RT_R = 16.7$)

in Figs. IV-41 and IV-42 (for simultaneous reactions) and Fig. IV-43 (for consecutive reactions). As is seen, an increase in residence time brings down the temperature level at which the reaction can proceed and raises the selectivity. At $b < 1$, in order to attain a high selectivity, the temperature level should be raised and the residence time should be cut down. At high fractional conversions, two extreme cases occur, one at low selectivity ($Q < 1000$, Figs. IV-41 and IV-42), with a single-kink S-curve, and the other at high selectivity ($Q > 1000$, Fig. IV-43), giving a double-kink S-curve.

Consider the stability of operating conditions for a polytropic well-stirred reactor.

High conversion, low selectivity. At high rates of conversion and low selectivity, the curve is generally similar to that for a single reaction, because the selectivity is so low that the two reactions proceed at practically the same temperature.

A stability plot for simultaneous reactions appears in Fig. IV-44 where the inlet temperature is T_0 and the desired operating point is at B. At this point, product R is predominant. Adiabatic conditions cannot exist at or

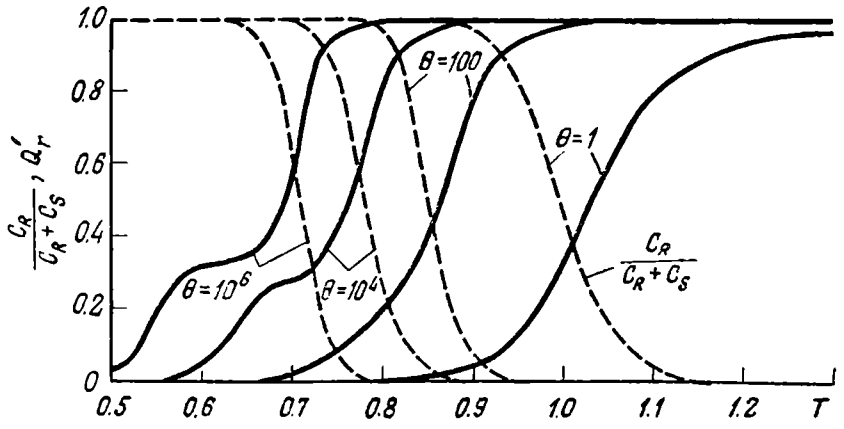


Fig. IV-43. Heat generation and yield in consecutive reactions as a function of residence time and reactor temperature ($H = 2$, $b = 2$, $E_1/RT_R = 16.7$)

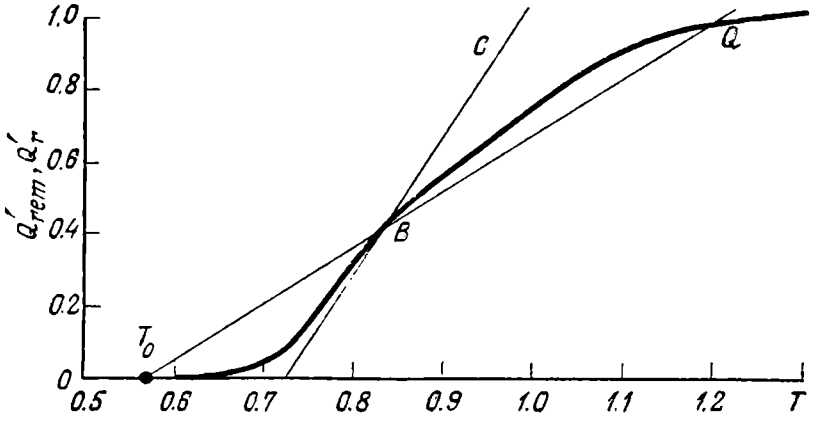


Fig. IV-44. Stability of polytropic well-stirred reactor carrying out simultaneous reactions ($\theta = 100$, $H = 2$, $b = 2$, $E_1/RT_R = 16.7$)

above point B, because the line connecting points T_0 and B defines a stable steady state only at T_0 and Q, but at Q the product S is predominant.

Thus, an unstable steady state exists at point B. The stability can be improved by cooling (the line of heat removal should be given a steeper slope), which fact is represented by point C, and the line, BC, represents a boundary case where a stable steady state is attained. However, there is a snag in this approach: the temperature of the heat-transfer medium has to be held higher than that of the inlet feed, and heat removal becomes dependent on the reactor load, that is. on the residence time, θ. As the residence time (load) and the inlet temperature are changed, however, the reactant concentration in the feed or the temperature of the heat-transfer medium must be changed more drastically in order to keep the yield constant.

The effect of changes in the load (residence time θ) on process control for consecutive reactions is illustrated in the plot of Fig. IV-45. It is assumed that the reactor is operating in the lower stable steady state at contact time $\theta = 1$. Halving the feed rate ($\theta \to 2$) results in the accumulation of an

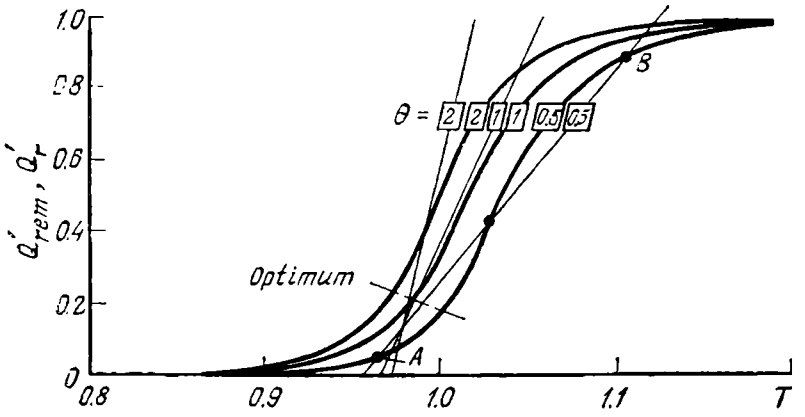


Fig. IV-45. Effect of load changes on reactor stability in consecutive reactions ($H = 2$, $b = 2$, $E_1/RT_R = 30$, $\Delta T_A = 1$, $T_0 = 0.850$, $T_f = 0.978$)

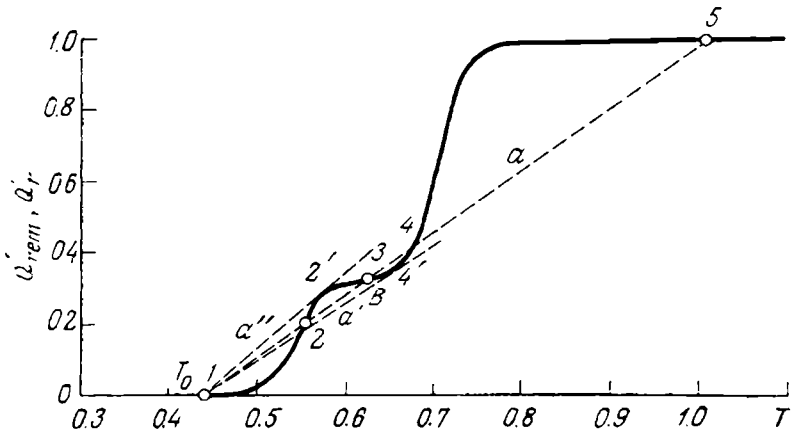


Fig. IV-46. Graphical determination of stability limits for adiabatic reactors carrying out consecutive reactions ($H = 2$, $b = 2$, $E_1/RT_R = 16.7$, $\theta = 10^6$)

unwanted product. Doubling the load ($\theta \to 0.5$) leads to three steady states. Depending on the dynamic behaviour of the reactor, two steady states can be stable. At point *A*, the fractional conversion is too low; at point *B* nearly all of the source reactant is turned to an unwanted product.

High conversion, high selectivity. A plot relating Q'_r and Q'_{rem} to reactor temperature appears in Fig. IV-46. As is seen, five steady states can exist, namely (1) a stable state (low conversion); (2) an unstable state (quenching leads to point *1*, and ignition to point 3); (3) a stable state (high fractional conversion to *R* and low fractional conversion to *S*); (4) an unstable state leading to point *3* or *5*; (5) a stable state (high fractional conversion to *S* and low fractional conversion to *R*).

It is desirable that the reactor be operating under the conditions existing at point *3*. If the reactant concentration in the feed be gradually increased, the slope of line *a* will decrease, point *3* will shift to the right and point *4* to the left. If line *a* be allowed to merge with line *a'*, points *3* and *4* will merge to form point *4'* at which a decrease or an increase in temperature

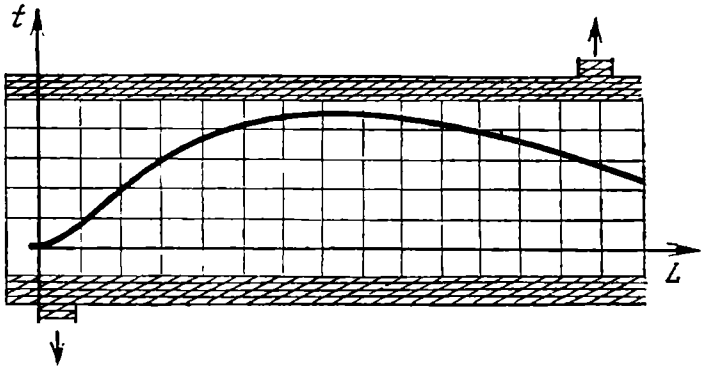


Fig. IV-47. Temperature profile in a tubular reactor

will result in a situation where heat generation will always exceed heat removal. The disturbances accompanying the rise in temperature will in the long run lead to a stable state at point *5* only. If the reactant concentration be reduced to values corresponding to line *a''*, the reactor will be completely quenched at point *2'*.

Tubular reactor. Consider a continuous tubular reactor with a double-pipe heat exchanger. In diagrammatic form, the distribution of temperature in the reaction zone with reactor length is shown in Fig. IV-47.

The temperature profile for this type of reactor is determined by the fact that the reactor volume within which the reaction generates heat is proportional to the diameter squared, while the heat transfer area is proportional to the first power of diameter. This is why in large-diameter pipes the instability is more pronounced than it is in small-diameter pipes. It should be borne in mind that, except autocatalytic reactions and reactions with an induction period, the maximum reaction rate at a given temperature is the initial rate, that is, one existing at the inlet to the reactor, and this condition is fraught with a dangerous rise in temperature.

Let the temperature, T, of the reaction mixture in a reactor be laid off as abscissa, and the heat per unit volume of reaction mixture per hour as ordinate. Then the resultant plot for a plug-flow reactor will have the shape shown in Fig. IV-48.

At first, the slope of the heat generation line increases because the temperature affects the reaction rate exponentially. On approaching the adiabatic temperature, the reaction rate tends to zero. At a constant jacket temperature and a constant heat transfer coefficient, the heat removal lines have a slope equal to $K_V F$ and intersect the axis of abscissae at a temperature, T_m, of the heat-transfer medium.

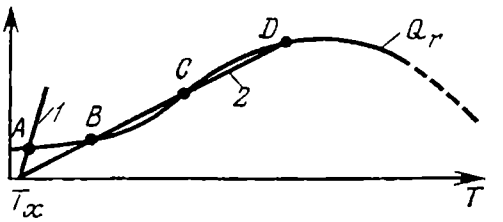


Fig. IV-48. Stability conditions for a tubular reactor

1, 2 — heat removal lines; Q_r = heat of reaction (heat-generation line)

Figure IV-48 illustrates two cases of heat transfer. Line *1* intersects the heat generation curve at point *A* at a maxi-

mum reaction rate. At point A, the process conditions are inherently stable, because a slight increase in the temperature of the reaction mixture will cause heat removal to rise at a higher rate than heat generation. A small drop in temperature will likewise result in self-regulation. Line *2* intersects the heat generation curve at points B, C and D. At points B and D, the process conditions are stable, while at point C they are unstable.

The stability of operating conditions at points A, B and D is explained by the fact that the heat removal line has a greater slope than the heat generation line, that is

$$dQ_{rem}/dT > dQ_{gen}/dT$$

The operating conditions at point D are of no practical importance, because the reaction is practically completed. If points B and C were spaced closely apart, the reactor would be operating within a potentially unstable region. A fast rise in jacket temperature would cause the heat removal line to shift to the right, the reactor temperature would rise from B to C, and this would result in a higher reactor temperature upon return of the jacket to its normal temperature. In such a case, a measure of process stability is the difference in temperature between B and C. This difference represents fluctuations in reactor temperature caused by changes in the flow rate or temperature of the heat-transfer medium, reactant inlet concentrations or flow rates.

A very important point in the heat-transfer calculations involved in reactor design is the choice of a correct temperature for the heat-transfer medium. Too low a temperature of the heat-transfer medium may stop a reaction altogether. Therefore, one should carry out a more detailed analysis with emphasis on thermal stability. An example of such an analysis follows.

Example IV-10. Assuming a first-order reaction, the volumetric velocity of the reactant is $V_q = 0.835$ m³/h, $c_0 = 3.2$ kmoles/m³, $(-\Delta H) = 54{,}428$ kJ/kmole = 13,000 kcal/mole. The initial temperature is 100°C. The temperature range of reactor operation is 110-120°C; above this temperature there is an increase in the amount of the unwanted products. The main process variables are summarized in Table IV-8.

Table IV-8

Temperature, °C	Rate constant, h^{-1}	Fractional conversion under adiabatic conditions, %	$Q_r = w_r(-\Delta H) = kc_0(1-x) \times(-\Delta H)$, kcal m^{-3} h^{-1} 10^{-3}
100	12	0	500
110	20	4	795
120	32	8	1220
130	54	12	1970
140	88	16	3080
150	132	20	4400
350	—	100	—

The data applicable to the inside pipe are presented in Table IV-9.

Table IV-9

Particulars	Diameter of inside pipe, mm		
	25	50	75
Area F_V, m^2/m^3	150	76.5	55
Heat-transfer coefficient, K_V, kcal m^{-2} h^{-1} deg^{-1}	1100	900	675
$K_V F_V \times 10^{-3}$	165	69	37.1

Solution. The amount of heat transferred to the heat-transfer medium is given by

$$Q_m = K_V F_V (T_R - T_m)$$

where T_R is the reactor temperature and T_m is the temperature of the heat-transfer medium.

The maximum difference in temperature, $T_R - T_m$, at a given reactor temperature, T_R, may be found from the above equation by substituting in it the values of $K_V F_V$ and replacing Q_m with the values of the heat of reaction at a given T_R from Table IV-8.

For the three pipe diameters listed in Table IV-9, the Q_r plots as a function of Q_m appear in Fig. IV-49. They are respectively labelled Q_{m1}, Q_{m2} and Q_{m3}.

25-mm pipe. At $T_R = 115$°C, the temperature of the heat-transfer medium will be $T_m = 110$°C. If T_m be raised to 115 °C, the maximum reactor temperature will be $T_R = 122$°C, and the operating conditions will remain stable. If variations in temperature are kept within 5°C, the reactor will operate under conditions of stability.

50-mm pipe. At $T_R = 115$°C or lower, the temperature of the heat-transfer medium should be about 101°C. If, however, T_m be raised to 105°C (see Fig. IV-49), the rate of heat removal will become equal to the rate of heat generation not until a temperature of 117°C is attained. This point is stable. Unfortunately, already at $T_m = 107$°C the process becomes unstable. To prevent the temperature of the heat-transfer medium from rising, a closer temperature control is important than with a 25-mm reactor pipe. The temperature of the heat-transfer medium must be kept constant to within ±2°C so that the "hot point" in the reactor be held anywhere between 110° and 120°C.

75-mm pipe. The difference in temperature is 20°C. The reactor cannot operate in the specified temperature range (110°-120°C). At $T_m = 91$°C, the lines of heat generation and heat removal intersect at 108°C. At $T_m = 92$ °C, they do so at 115°C. The range of allowable changes in temperature reduces to ±1°C.

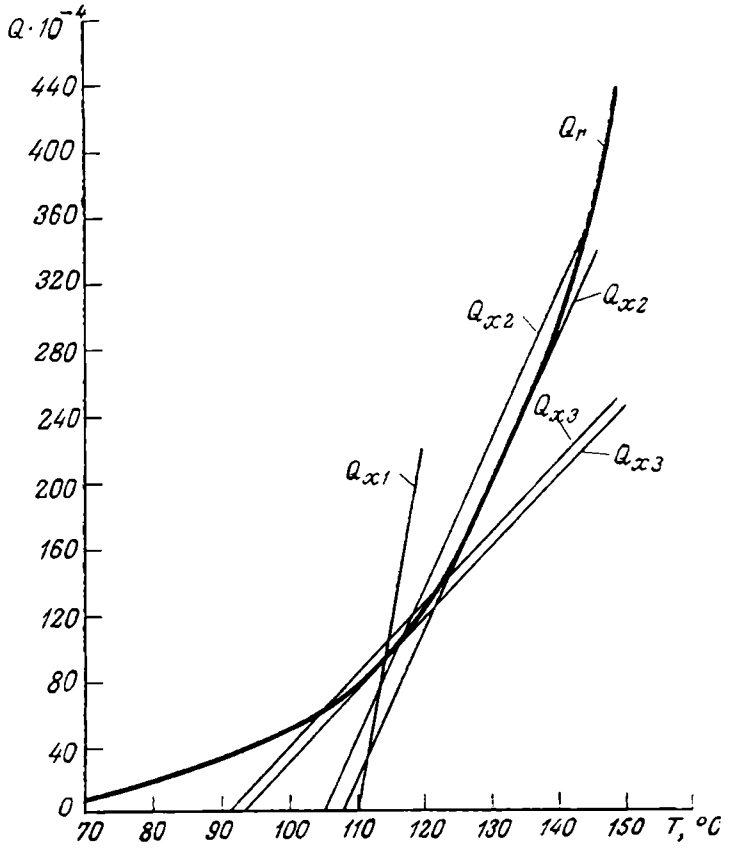


Fig. IV-49. To the calculation of a polytropic reactor

In the light of the foregoing, the rule for determining the critical temperature difference, $\Delta T_c = T_R - T_m$, according to the fractional conversion may be stated as follows: ΔT_c is inversely proportional to fractional conversion per degree. For example, at a fractional conversion of 5% per degree C, $\Delta T_c = 1/0.05 = 20°C$. At $x = 8\%$ per degree C, $\Delta T_c = 1/0.08 = 12.5°C$.

Use of a controller. With a controller incorporated in the system, stable operating conditions can be maintained by increasing the slope of the heat removal line with a rise in T_R through a reduction in the jacket temperature and an increase in the flow rate of the heat-transfer medium.

For an unsteady state, the differential equation of the reactor may be written as

$$\rho g c_p \frac{dT_R}{d\tau} = \frac{dQ_r}{dT_R} T_R - K_V F_V (T_R - T_m) \qquad \text{(IV-226)}$$

Equation (IV-226) may be re-written as follows

$$\left(\frac{\rho g c_p}{K_V F_V - \frac{dQ_r}{dT_R}} \right) \frac{dT_R}{d\tau} + T_R \frac{K_V F_V T_m}{K_V F_V - \frac{dQ_r}{dT_R}} \qquad \text{(IV-227)}$$

Putting

$$T = \frac{\rho g c_p}{K_V F_V - \frac{dQ_r}{dT_R}} \qquad K_R = \frac{K_V F_V}{K_V F_V - \frac{dQ_r}{dT_R}}$$

Then

$$T\frac{dT_R}{d\tau} + T_R = K_R T_m \tag{IV-228}$$

Taking the Laplace transform, we get

$$TT_R p + T_R = K_R T_m$$

whence

$$T_R/T_m = K_R/(T_p + 1) \tag{IV-229}$$

The pseudo-time constant, T, of the reactor becomes very large as dQ_r/dT_R approaches $K_V F_V$; this is an indication that under these conditions the reactor will approach its stable operating point very slowly.

Let us use a proportional controller which changes the jacket temperature by ΔT_m in proportion to change, ΔT_R, in the reactor temperature and has a gain K_C:

$$K_C = -\Delta T_m/\Delta T_R = (T_{m0} - T_m)/(T_R - T_{R0}) \tag{IV-230}$$

$$T_m = T_{m0} - K_C(T_R - T_{R0}) \tag{IV-231}$$

where the subscript "0" applies to the specified normal conditions.

Since the overall gain is the product of the gain of the control system (comprising a sensor, a controller, a control valve and a jacket) by the reactor gain, K_R, it is seen that the slope of the heat removal line and, as a consequence, the critical difference in temperature may be increased. Then the amount of heat removed will be

$$Q_m = K_V F_V(T_R - T_m) = K_V F_V[T_R(K_C + 1) - T_{m0} - K_C T_{R0}] \tag{IV-232}$$

Thus, a proportional controller increases the slope of the heat removal line by a factor of $(K_C + 1)$.

IV-10. DETERMINING AN OPTIMUM TEMPERATURE PROFILE FOR POLYTROPIC REACTORS

In contrast to isothermal reactors where the temperature remains constant as a reaction proceeds and to adiabatic reactors where any change in temperature is uniquely related to the fractional conversion and the heat of reaction, in polytropic reactors the temperature may vary independently of the heat of reaction and fractional conversion in any manner.

Accordingly, there rises a problem of optimizing polytropic reactors in terms of temperature, that is, a problem of finding an optimum temperature profile (in time or space) with which the process can be maintained at the highest possible rate at any instant of time or in any cross-section of a tubular reactor.[16]

As an example, consider an optimum strategy for temperature control in the case of a first-order reversible reaction proceeding to the scheme

$$A \rightleftarrows R \qquad \text{(IV-233)}$$

described by a rate equation of the form $w_r = c_{A0}(dx_A/d\tau) = k_{01} \exp(-E_1/RT)c_{A0}(1-x_A) - k_{02} \exp(-E_2/RT)c_{A0}x_A$ where c_{A0} is the inlet concentration of reactant A, x_A is the fractional conversion of reactant A, E_1 and E_2 are the activation energies for the forward and reverse reactions, respectively, k_{01} and k_{02} are the pre-exponential factors of the rate constants for the forward and reverse reactions, R is the universal gas constant, and T is the absolute temperature.

An optimum temperature corresponding to an arbitrary fractional conversion x_A may be found by taking a temperature derivative of the reaction rate and equating it to zero:

$$\partial w_r/\partial T = c_{A0}(1-x_A)k_{01}E_1 \exp(-E_1/RT) - c_{A0}x_A k_{02}E_2 \exp(-E_2/RT) = 0 \qquad \text{(IV-234)}$$

$$T_{opt} = \frac{E_2 - E_1}{R \ln\left[\dfrac{E_2 k_{02} x_A}{E_1 k_{01}(1-x_A)}\right]} \qquad \text{(IV-235)}$$

where T_{opt} is the optimum temperature.

The dependence of the optimum temperature on the fractional conversion can similarly be found for second- and third-order reversible reactions.

It is convenient to write Eq. (IV-235) as follows:

$$1/T_{opt} = \ln(A_2A_3)/A_1 \qquad \text{(IV-235}a\text{)}$$

where $A_1 = (E_2-E_1)/R$, $A_2 = k_{02}E_2/k_{01}E_1$, and A_3 is a function of x_A the form of which depends on the type and order of the reversible reaction.

(a) For a first-order reaction

$$A_3 = x_A/(1-x_A)$$

(b) for a second-order reaction of the type $A+B \rightleftarrows R-S$

$$A_3 = x_A^2/(1-x_A)(M-x_A)$$

(c) for a second-order reaction of the type $A \rightleftarrows R+S$

$$A_3 = c_{A0}x_A^2/(1-x_A)$$

(d) for a second-order reaction of the type $A+B \rightleftarrows R$

$$A_3 = x_A/(1-x_A)(M-x_A)c_{A0}$$

where $M = c_{B0}/c_{A0}$.

When plotted on semi-logarithmic coordinates, Eq. (IV-236) yields a straight line with a slope equal to A_1^{-1}.

Thus, once A_1 and A_2A_3 have been found for a set of values of x_A in the interval from 0 to a finite fractional conversion, x_{Ak}, we may plot Eq. (IV-236) on the $T_{opt} - x_A$ coordinates, find optimum temperatures by

connecting the points corresponding to T_{opt} and x_A, and determine the sought dependence of T_{opt} on x_A (Fig. IV-50).

It should be borne in mind that the initial temperature is always subject to constraints of economical or engineering nature.

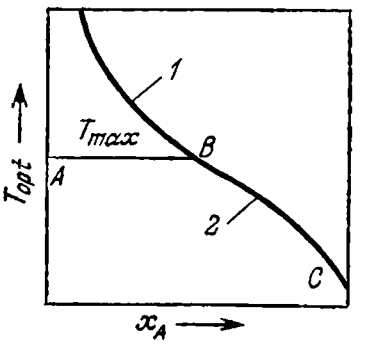


Fig. IV-50. To the calculation of an optimum temperature
1 – theoretical curve; *2* – limit line

Example IV-11. Map out an optimum strategy for changes in temperature with changes in fractional conversion and residence time for a first-order reversible reaction of the type $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$ carried out in a batch reactor. Given: the pre-exponential factors $k_{01} = 69.5$ min^{-1} and $k_{02} = 5555.0$ min^{-1}, the activation energies $E_1 = 5556$ kcal kg^{-1} mole^{-1} and $E_2 = 1112$ kcal kg^{-1} mole^{-1}. The limit of temperature is 532°K. The desired fractional conversion for the reactant is 0.8.

Solution. To begin with, we choose a set of values for x_A in the interval from 0 to 0.8 and solve Eq. (IV-235) for the respective optimum temperature:

x_A	0	0.15	0.20	0.40	0.60	0.80
T_{opt}, °K	805	805	750	595	510	430

The optimum strategy for temperature control can then be found by either numerical or graphical integration of Eq. (IV-233). The results are tabulated below:

x_A	0	0.15	0.20	0.40	0.60	0.80
τ, min	0	0.1	0.2	0.7	3.0	11.0
T, °K	805	805	750	595	510	430

IV-11. AUTOTHERMAL REACTORS

Reactors in which the heat of reaction is utilized to heat the reactants are called *autothermal*. It may be so arranged that a process will be maintained at some predetermined temperature as if automatically, that is, under autothermic conditions.

Consider an adiabatic tubular reactor with a heater (Fig. IV-51).[17] From a heat balance around the reactor adjusted for the adiabatic temperature, T_a, we have

$$T_f - T_0 = x_A T_a \qquad \text{(IV-236)}$$

A heat balance around the heater is

$$V_q \rho g c_p (T_0 - T_0') = K_V F (T_f - T_0) \qquad \text{(IV-237)}$$

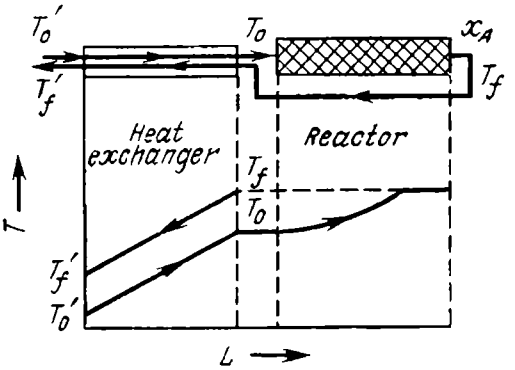


Fig. IV-51. Sketch of an adiabatic reactor with a heater

Substituting Eq. (IV-236) into Eq. (IV-237) gives

$$T_0 - T_0' = x_A T_a \frac{K_V F}{V_q \rho g c_p} \qquad \text{(IV-238)}$$

From the last equation it follows that the temperature of the feedstock will rise by an amount equal to the rise in the reactor temperature, multiplied by $(K_V F)/(V_q \rho g c_p)$. In practice, this factor is often greater than unity.

The left-hand side of Eq. (IV-238) is proportional to the amount of heat exchanged in the heater per unit volume of feed, while the right-hand side is proportional to the amount of heat generated by the reaction. The two quantities may be plotted as functions of the inlet temperature, T_0, which is the limiting variable in this case. The intersections of the two curves

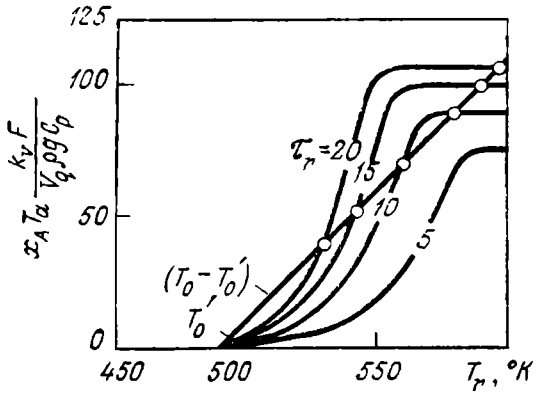


Fig. IV-52. Operating conditions for an autothermal reactor

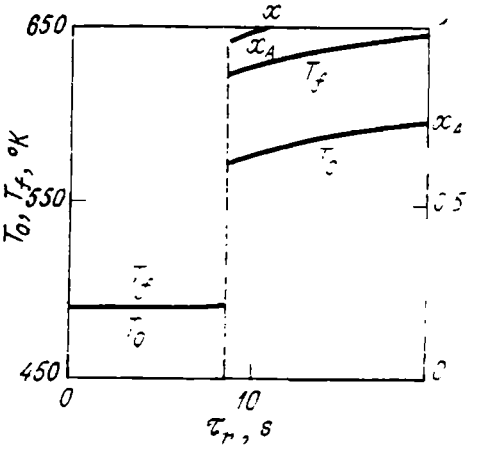


Fig. IV-53. Fractional conversion, inlet and outlet temperatures as functions of residence time for an autothermal reactor

define the likely operating conditions for the system. Figure IV-52 gives such a plot for a first-order reaction at different residence times, τ_r, inversely proportional to the volumetric throughput, V_q. The overall heat transfer coefficient, K_V, has been taken proportional to $V_q^{3.4}$.

A plot of inlet and outlet temperatures as functions of residence time under similar conditions is shown in Fig. IV-53. As is seen, stable operating conditions at high fractional coversion are only possible above certain values of residence time. Under such conditions, the temperature level of the reactor is more sensitive to loading. If the volumetric velocity of the reactants in a system is increased, the reaction will slow down at some value of τ_r, as may be seen from the plot of Fig. IV-53 at $\tau_r \approx 8.6$ s.

The principle of an autothermal reactor is widely utilized in catalytic-converter processes. In Fig. IV-54 is a sketch of an autothermal reactor for ammonia synthesis. In the reactor, heat is exchanged between the reaction stock and the cold feed. The relevant material and heat balances may be set up as follows:

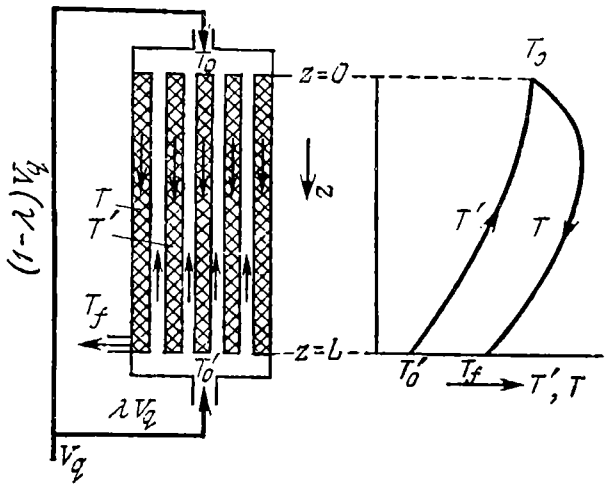


Fig. IV-54. An autothermal multi-tubular reactor with an internal heat exchanger

—around the heating zone:

$$\lambda V_q \rho g c_p \, dT' + K_V (T - T') (F/L) \, dz = 0 \qquad \text{(IV-239)}$$

— around the reaction zone:

$$V_q \rho g c_p \, dT - V_q (-\Delta H) c_{A0} \, dx_A + K_V (T - T') (F/L) \, dz = 0 \qquad \text{(IV-240)}$$

— the boundary conditions are defined as

$$\begin{aligned} T' &= T_f' && \text{at} \quad z = L \\ T = T_0 &= (1-\lambda) T_f' + \lambda T_0' && \text{at} \quad z = 0 \\ x_A &= 0 && \text{at} \quad z = 0 \end{aligned} \qquad \text{(IV-241)}$$

The problem is solved on a computer for various values of $T_a(K_V/F)/(V_q \rho g c_p)$ and λ.

For a qualitative evaluation of the above autothermal system, the problem may be simplified by putting $\lambda = 1$. On introducing the adiabatic temperature, we get

$$T - T' = T_a x_A$$

Substituting the above expression for $T - T'$ in Eq. (IV-239), we obtain

$$V_q \rho g c_p \, dT' / K_V F = (-T_a/L) x_a \, dz \qquad \text{(IV-242)}$$

On integrating between the limits $z = 0$ and $z = L$, we get

$$\frac{T_0 - T_f'}{(K_V F)/(V_q \rho g c_p)} = \frac{T_a}{L} \int_0^L x_A \, dz = T_a \bar{x}_A \qquad \text{(IV-243)}$$

where $\bar{x}_A$ is the average fractional conversion along the reactor length and $T_a \bar{x}_A$ is the average driving force of heat transfer.

For a given system, $\bar{x}_A$ is a function of both T_0 and $(K_V F)/(V_q \rho g c_p)$, and for equilibrium (reversible) reactions it passes through a maximum depen-

dent on T_0. The overall rise in feed temperature is equal to the product of the average driving force $T_a\bar{x}_A$ by the factor $(K_VF)/(V_q\rho gc_p)$.

A plot of both factors as a function of temperature T_0 at the inlet to a catalyst bed for a set of values of $(K_VF)/(V_q\rho gc_p)$ is shown in Fig. IV-55. As is seen, the value of $(K_VF)/(V_q\rho gc_p)$ affects the slope of both the heat generation and heat removal lines. At low rates of heat exchange, that is

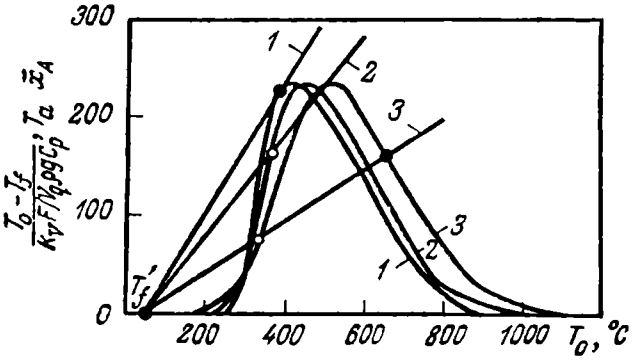


Fig. IV-55. Operating conditions for ammonia synthesis
1 — $K_VF/V_q\rho gc_p = 1.6$; *2* — $K_VF/V_q\rho gc_p = 2$; *3* — $K_VF/V_q\rho gc_p = 4$

at low values of $(K_VF)/(V_q\rho gc_p)$, the inlet temperature will be too low and the reaction will fail to start at all (line *1*). Conversely, at high values of $(K_VF)/(V_q\rho gc_p)$, the reaction temperature (curve *3*) will be too high, and a reverse reaction will set in.

To sum up, in designing an autothermal reactor, it is important to judiciously choose the value of $(K_VF)/(V_q\rho gc_p)$ and not to overlook the effect of pipe diameter examined earlier. For example, with too large an area, F, some of the cold feed may have to be bypassed ($\lambda < 1$) directly into the catalyst bed. Since the heat-exchange surface is contaminated or the surface of the catalyst bed becomes less active with time, the value of λ has to be gradually raised so as to maintain the fractional conversion at a constant level.

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CHAPTER V

CHEMICAL KINETIC EXPERIMENTS AND INTERPRETATION OF LABORATORY KINETIC DATA

Laboratory-scale studies of a chemical process have as their objectives to establish the kinetics of the process, reaction paths, and an optimum breakdown of intermediate products in complex reactions.

Since a chemical reaction is accompanied by interactions of the reacting species at the molecular level, it is assumed that the process proceeds at the molecular, or microscopic, level. The rates of processes at the molecular level constitute process microkinetics.

Microkinetics is investigated in a manner completely eliminating the disturbing effect of macroscopic events, such as mixing, temperature profiles, and concentration profiles due to the side effects of diffusion. This is why, in its pure form, the kinetics of chemical reactions is investigated by specially designed methods and techniques in specially designed reactors (to be discussed later). The observer usually works in a "closed loop" with a computer which can readily evaluate the kinetic data obtained by experiment. These kinetic data are an essential element (block) of an overall mathematical model of an industrial process.

With elementary reactions, it is a simple matter to ascertain the mechanism and rate of reactions, because their stoichiometric equations uniquely define the respective mathematical models.

With reactions other than elementary, where the stoichiometric coefficients are no longer correlated with the mathematical model of the reaction rate, the investigator has to hypothesize the mechanism of a complex reaction as a sequence of simple reactions and then to test the experimental data found from the reaction rate for goodness of fit to the assumed reaction mechanism.

Kinetic data on homogeneous liquid systems are usually derived from experiments conducted in a batch reactor or, more seldom, in a continuous reactor. For heterogeneous systems, and reactions taking place in a gas phase, kinetic data are obtained in continuous (tubular) reactors, over a

small length of a catalyst bed (differential reactors), or over the entire length of a catalyst bed (integral reactors, so called because the response is an integral of the process rates over all elementary volumes of the apparatus), or in recycle units.

For a closed system, kinetic data are derived by measuring time dependence of a chemical or physical observable which is a function of concentration. These data may be written in any one of three forms:

(1) Rate of change of concentration, c, as a function of time, τ:

$$dc/d\tau = f(\tau)$$

(2) Rate of change of concentration, c, as a function of concentration:

$$dc/d\tau = f(c)$$

(3) Concentration, c, as a function of time, τ:

$$c = f(\tau)$$

In the past, rate-*vs*-time data were used but seldom. Today, with the advent of continuous recorders which can measure rates while a reaction is in progress, the method based on these data has come to be used on a far wider scale. In principle, rate-*vs*-concentration data are more useful, because they may be directly used in equations of differential rates (which is the reason why the method is called "differential").

Simulation on analog computers greatly speeds up the choice of constants for kinetic equations.

As already noted, kinetic data for homogeneous reactions are usually collected by experiments in stirred batch reactors. Changes in concentration can be either measured directly or inferred indirectly from changes in some physical properties (system volume or pressure, electric conductivity, refraction, and the like).

The experimental data thus obtained are then plotted, with the concentration, c, as ordinate and the reaction time, τ, as abscissa (Table V-1).

Thus, the first step in laboratory kinetic studies for homogeneous systems is to ascertain the manner in which the concentration of the reactant varies with time at a fixed temperature. The second step is to interpret the experimental relationships, $c = f(\tau)$, in order to find kinetic constants, namely the specific reaction rate and the reaction order, that is, the power exponents of the reactant concentrations. This can be done by two methods, integral and differential.

V-1. INTEGRAL METHOD

The integral method is used to test the rate equation based on plausible mechanisms to confirm the mechanism and order of reactions by integrating and checking the assumed concentration-time history against the experimental kinetic data. The integral method is particularly suitable for reactions which come close to elementary ones. The procedure is as follows.[1]

Table V-1

Concentration-Versus-Time and $F(c_A)$ Plots for Typical Reactions at Constant Volume

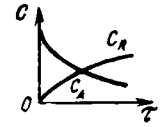
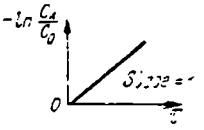
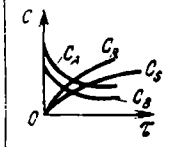
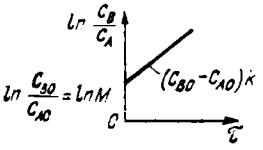
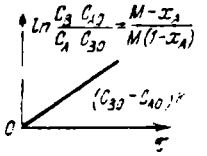
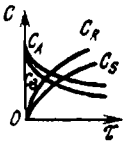
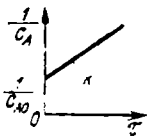
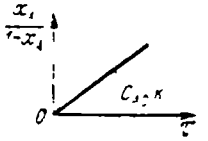
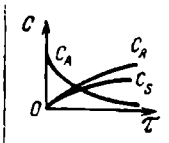
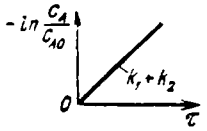
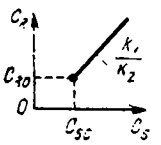
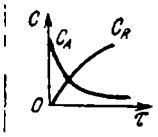
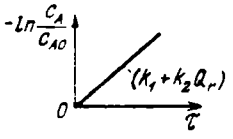
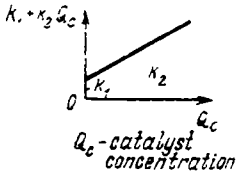
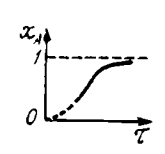
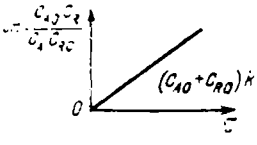
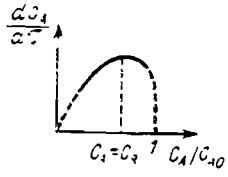
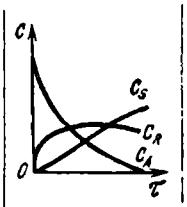
Reaction type and order	Plot of c–vs–τ	Plot of $F(c_A) = \int_{c_{A0}}^{c_A} f(c_A)^{-\tau}$
Simple Reactions		
$A \xrightarrow{k} R$; $n = 1$		
$A+B \xrightarrow{k} R+S$; $n = 2$		 
$A = B$ or $2A \rightarrow R+S$; $n = 2$		 
Simultaneous Reactions		
$A \xrightarrow{k_1} R$ $A \xrightarrow{k_2} S$		 
Homogeneous Catalysis		
$A \xrightarrow{k_1} R$ $A+Q \xrightarrow{k_2} R+Q$		 
Autocatalytic Reactions		
$A - R \xrightarrow{n} R+R$		 

Table V-1 (continued)

Reaction type and order	Plot of c-vs-τ	Plot of $F(c_A) = \int_{c_{A_2}}^{c_A} f(c_A)^{-\tau}$

Consecutive Reactions

$A \xrightarrow{k_1} R \xrightarrow{k_2} S$



$$c_{A0} = c_A + c_R + c_S$$

$$c_R = c_{A0} k_1 \left(\frac{e^{k_1 \tau}}{k_2 - k_1} + \frac{e^{-k_2 \tau}}{k_1 - k_2} \right)$$

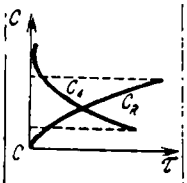
$$c_S = c_{A0} \left(1 + \frac{k_2}{k_1 - k_2} e^{-k\tau} + \frac{k_1}{k_2 - k_1} e^{-k\tau} \right)$$

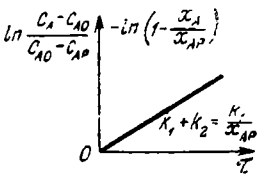
$$\frac{c_{R,\max}}{c_{A0}} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}};$$

$$\tau_{\max} = \frac{\ln (k_2/k_1)}{k_2 - k_1}$$

Reversible Reactions

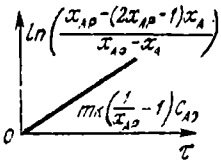
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R; \quad n = 2$





$$x_{Ap} = \frac{K_c - c_{R0}/c_{A0}}{K_c + 1}$$

$$K_c = \frac{K_1}{K_2} = \frac{c_{Rp}}{c_{Ap}}$$



$A - B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$

$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$

$m = 2$

$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S; \quad m = 1$

$A - B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R; \quad m = 4$

Note. n = reaction order

$M = c_{B0}/c_{A0}$

$x_A = (c_{A0} - c_A)/c_{A0}$

Q_c = catalyst concentration

(1) The rate equation is written in a form applicable to the postulated reaction mechanism.

At constant volume, the kinetic equation is

$$w_{rA} = -dc_A/d\tau = f_0(kc) \tag{V-1}$$

where w_{rA} is the reaction rate with respect to reactant A, k is the velocity constant, and c_A is the concentration of reactant A.

Assuming that k is independent of concentration we may write

$$-w_{rA} = -dc_A/d\tau = kf(c) \tag{V-2}$$

(2) Equation (V-2) is then re-written as

$$-dc_A/f(c) = kd\tau \tag{V-3}$$

Now the function $f(c)$ involves only concentration and can be expressed in terms of c_A. Therefore, Eq. (V-3) may be integrated

$$-\int_{c_{A0}}^{c_A} dc_A/f(c_A) = F(c_A) = k\int_0^{\tau} d\tau = k\tau \tag{V-4}$$

(3) From the reactant concentrations found by experiment, we then evaluate $F(c_A)$ for a set of values of τ. If the integral on the left-hand side of Eq. (V-4) cannot be evaluated directly, graphical integration is used, and the area under the $1/f(c_A)$-*vs*-c_A curve is determined.

(4) The values of $F(c_A)$ thus found are then plotted against time. If the plot yields a straight line, the postulated mechanism fits the experimental data. If, on the other hand, the curve is other than a straight line, another mechanism has to be assumed, new calculations made, and a new plot constructed. This procedure is repeated until the plot yields a straight line (see Table V-1).

(5) If no straight line is obtained after all, other mechanisms and other kinetic equations must be considered.

(6) If the reaction under study proceeds by an elementary mechanism, the integral may be taken directly by Eq. (III-34) for the postulated reaction order.

A criterion of whether a correct kinetic equation has been chosen is the grouping of experimental data near the τ-*vs*-$F(c_A)$ curve. The integrated forms of applicable equations for several types of reactions are presented in Table V-1.

Using the plots of Table V-1, we can readily deduce the analytical relationship, $F(c_A)$ versus τ, the left-hand side of which is the ordinate, and the right-hand side is the product of the slope by time τ. For example, for a reaction of the type $A \xrightarrow{k} R$ at $n = 1$, we have:

$$-\ln c_A/c_{A0} = k\tau$$

For irreversible nth order reactions for which

$$-dc_A/d\tau = kc_A^n \tag{V-5}$$

at $n \neq 1$, integration yields

$$(c_A^{1-n} - c_{A0}^{1-n}) = (n-1)k\tau \qquad \text{(V-6)}$$

To deduce the velocity constant and the reaction order n, Eqs. (V-5) and (V-6) are solved by the method of successive approximations. To begin with, a value is assumed (guessed) for n, and that of k is found. The value of n that minimizes the change in the velocity constant k gives the sought reaction order.

Half-life method. This method consists in determining the time taken for the initial concentration of a reactant to be reduced by a factor of two, $\tau_{1/2}$. Then, integration of Eq. (V-5) gives

$$\tau_{1/2} = \frac{2^{n-1}-1}{k(n-1)} c_{A0}^{1-n} \qquad \text{(V-7)}$$

Then, Eq. (V-7) is plotted on logarithmic coordinates for various reaction orders (Fig. V-1). The plot thus obtained can be used to test the kinetic equations against the results of kinetic experiments. These results should appear grouped at the respective straight line. Experiments are carried out at two or more different initial concentrations for each reactant.

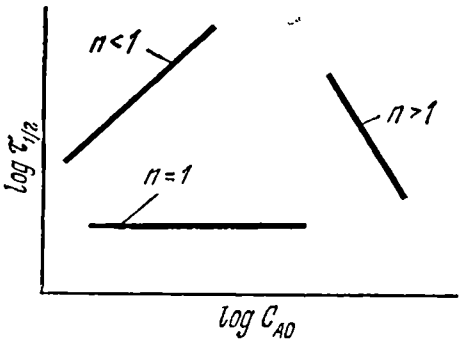


Fig. V-1. Half-life as a function of initial concentration for different order reactions

In cases where the reactions under study have complex kinetics, the assumed rate equations are tested by parts. Accordingly, different techniques of experiment have to be used,[1] notably: (1) the exclusion method; (2) the method of initial rates and (3) the isolation method.

Exclusion method. Let there be a non-elementary reaction of the type

$$aA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} rR + sS$$

for which the following kinetic equations may be assumed:

$$-dc_A/d\tau = k_1 c_A^a - k_2 c_R^r c_S^s$$
$$-dc_A/d\tau = (k_1' c_A - k_2' c_R^r c_S^s)/(1 + k_3' c_s)$$

Experiments are carried out, starting with only reactant A and terminating well before appreciable amounts of products (say, R and S) form. Then, the complete equation is analysed by parts for the reactant:

$$-dc_A/d\tau = k_1 c_A^a \text{ and } -dc_A/d\tau = k' c_A$$

Similarly, experiments are carried out, starting with pure R and S if the reaction is reversible

$$aA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} rR + sS$$

and terminating before an appreciable amount of A appears:

$$dc_R/d\tau = k_2 c_R^r c_S^s$$

$$dc_R/d\tau = k_2' c_R^r c_S^s/(1+k_3' c_s)$$

Method of initial rates. Experiments are carried out in a differential reactor, which implies that measurements are made for a small difference in concentration, and the derivative is approximated by a finite small increment. Then

$$\Delta c_A/\Delta\tau = k_1 c_A^a$$

From a series of experiments with varying concentrations of reactant A and at negligible concentrations of products R and S, one deduces the values of k_1 and a. Thus, instead of causing concentrations to vary with time, one determines the initial rates under various initial conditions, which calls for a very high accuracy in measuring concentrations (refer to p. 391 for application of this method to catalytic-contacting processes).

Isolation method. In making experimental observations of conversion with time, it is arranged that all of the reactants except one are present in excess. Hence, in the course of the reaction the concentration of this reactant will change markedly while those of the reactants present in excess will remain practically unchanged. Thus, the kinetic equation will be reduced in such experimentation to

$$-(dc_A/d\tau) = k(c_{B0}^b \ldots)c_A^n \approx kc_A^n$$

The data thus obtained are then plotted on logarithmic coordinates to yield a straight line with a slope n.

V-2. DIFFERENTIAL METHOD

The differential method is used to test differential kinetic equations directly, without integrating them. With simple reactions, an equation as a whole is tested; with more complex reactions, this is done by parts, which are then combined to get the complete equation. Analysis by the differential method may be carried out on analog computers.

The sequence of steps in the analysis of kinetic experiments by the differential method is as follows.

(1) According to the mechanism assumed, the kinetic reaction is written as

$$w_{rA} = -(dc_A/d\tau) = f_0(kc)$$

$$w_{rA} = -(dc_A/d\tau) = kf(c)$$

(2) $-(dc_A/d\tau)$ is evaluated from the c-vs-τ curves for a set of values of τ.

(3) The reactant concentrations, product concentrations and values of $-(dc_A/d\tau)$ for the chosen increments of time are then tabulated.

(4) The tabulated data are then plotted, with $(dc_A/d\tau)$ as ordinate and $f(c)$

as abscissa. If the plot yields a straight line passing through the origin of coordinates, the postulated rate equation fits the experimental data.

In the use of the differential method, it is sometimes convenient to take a logarithm of the differential equation and to construct a logarithmic plot with the reaction rate w_r as ordinate and the concentration c as abscissa. Let there be a reaction of the type

$$aA+bB \rightarrow \text{Products}$$

Then, the differential rate equation will be of the form

$$-w_{rA} = dc_A/d\tau = kc_A^a c_B^b$$

Putting $a+b = n$ and $[c_A] = [c_B]$, we may write

$$-w_{rA} = k[c_A]^n$$

Next, $(-w_{rA})$ is evaluated from the plot of concentration versus time, by differentiating the experimental $c_A = f(\tau)$ curve, and the above equation is plotted (Fig. V-2*a*) with $\log(-w_{rA})$ as ordinate and $\log(c_A)$ as abscissa. The slope of the resultant curve gives the overall reaction order, n, and the intercept on the ordinate axis, the velocity constant, k.

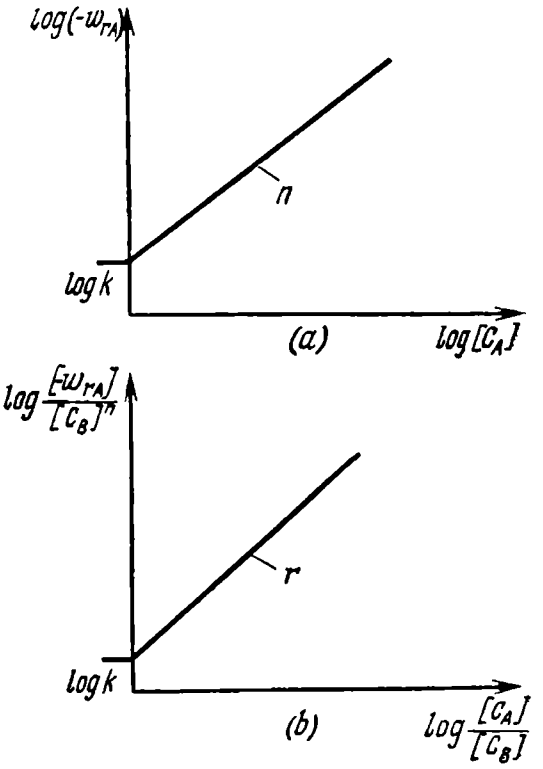


Fig. V-2. Finding kinetic constants by taking logarithms of kinetic equations

(*a*) finding the overall reaction order; (*b*) finding the reaction order with respect to a reactant

Once the overall reaction order, n, is deduced, we can readily determine the reaction order with respect to each reactant. In such experimentation, however, $[c_A] \neq [c_B]$. As a way out, the original equation may be re-written as

$$-w_{rA} = k[c_A]^a [c_B]^b = k[c_A]^a [c_B]^{n-a} = k[c_B] \left\{\frac{[c_A]}{[c_B]}\right\}^a$$

Taking a logarithm of the last equation, we get

$$\log \frac{[-w_{rA}]}{[c_B]^n} = \log k + a \log \frac{[c_A]}{[c_B]}$$

Then we plot the above equation (Fig. V-2*b*), with the left-hand side laid off as ordinate, and the last term on the right-hand side as abscissa The plot yields a straight line with a slope equal to the reaction order with respect to reactant A. The reaction order with respect to reactant B is found from the difference

$$b = n-a$$

As an alternative, the reaction order with respect to each reactant and the velocity constant may be derived by the *least squares method*. In such a case, after taking a logarithm, the original equation is reduced to the form.

$$\log(-w_{rA}) = \log k + a \log [c_A] + b \log [c_B]$$

which corresponds to a regression equation

$$y = a_0 + ax_1 + bx_2$$

Another technique convenient in estimating the reaction order is by taking a logarithm of the kinetic equation expressed in terms of fractional conversion

$$dx/d\tau = kc_0^{n-1}(1-x)^n = k'(1-x)^n$$

whence

$$\log(dx/d\tau) = \log k' + n \log(1-x)$$

A plot of the logarithm of reaction rate versus the logarithm of fractional conversion yields a straight line whose slope defines the reaction order. An advantage of this method is that it is applicable to reactions of a fractional order and that it gives initial rates. This method is still more advantageous than any other if the reaction order is subject to change in the course of a process. A limitation of this method is that it calls for a great number of precise data.

The effect of change in volume. As regards kinetic studies in a variable-volume batch reactor, Levenspiel[1] has proposed a technique for experimental data analysis, assuming a linear change in volume. Thus, postulating that the system volume varies linearly with fractional conversion, we may write

$$V = V_0(1+\delta_A x_A) \tag{V-8}$$

where

$$\delta_A = \frac{V_{x_A=1} - V_{x_A=0}}{V_{x_A=0}} \tag{V-9}$$

Noting that a change in the moles of reactant A may be expressed in terms of fractional conversion x_A as

$$N_A = N_{A0}(1-x_A)$$

and using Eq. (V-8), the concentration c_A may be written as

$$c_A = \frac{N_A}{V} = \frac{N_{A0}(1-x_A)}{V_0(1+\delta_A x_A)} = c_{A0}\frac{1-x_A}{1+\delta_A x_A} \tag{V-10}$$

The last expression is then substituted in that for the reaction rate

$$w_{rA} = -\frac{dc_A}{d\tau} = -\frac{d}{d\tau}\left(c_{A0}\frac{1-x_A}{1+\delta_A x_A}\right) = \frac{c_{A0}}{1+\delta_A x_A}\frac{dx_A}{d\tau} \tag{V-11}$$

Similarly, for any nth order, we get

$$\frac{c_{A0}}{1+\delta_A x_A}\frac{dx_A}{d\tau} = kc_A^n \tag{V-12}$$

$$\frac{c_{A0}}{1+\delta_A x_A}\frac{dx_A}{d\tau} = kc_{A_0}^n\left(\frac{1-x_A}{1+\delta_A x_A}\right)^n \tag{V-13}$$

whence

$$k\tau = c_{A_0}^{1-n}\int_{x_A=0}^{x_A}\frac{(1+\delta_A x_A)^{n-1}}{(1-x_A)^n}\,dx_A \tag{V-14}$$

The above integral for any reaction order can be evaluated graphically. Using the results of kinetic experiments in a batch reactor, Wright[2] has deduced velocity constants for a complex first-order consecutive-simultaneous reaction without assuming the linearity of change in system volume.

V-3. DEDUCTION OF REACTION ORDER BY A DIFFERENTIAL-INTEGRAL METHOD (METHOD OF TIME RATIOS)

This method is in effect a method of increments and combines the advantages offered by the differential and integral methods.[3] It may be applied to testing postulated initial conditions and stoichiometry. In many cases, it may suggest the form of a more complex expression for reaction rate, that would fit experimental data. By using a few simple approximations to a time-versus-concentration plot for one experiment, it is possible to deduce important information about the kinetics of a process.

The ratio of the time interval needed to reach a particular reaction percentage (conversion) to that needed to reach another reaction percentage (conversion) is deduced from the following two equations:

$$\ln(1-x) = -k\tau \quad n = 1 \tag{V-15}$$

$$\frac{c_0^{1-n}(1-x)^{1-n}-1}{1-n} = -k\tau \quad n \neq 1 \tag{V-16}$$

developed on integrating the equation

$$dx/d\tau = kc_0^{n-1}(1-x)^n$$

The ratio of the time interval needed to reach one reaction percentage (conversion) to that needed to each another (assuming the same initial reactant concentration, c_0) deduced from Eqs. (V-15) and (V-16) will be fixed numerically for the same values of n. For example, for $n = 3$ at τ_{60} and τ_{20} (where τ_{60} and τ_{20} give the time needed to reach 60% and 20% completion), we have

$$-k\tau_{60}/-k\tau_{20} = \tau_{60}/\tau_{20} = (0.4^{1-3}-1)/(0.8^{1-3}-1) = 9.333$$

The conversion time ratios deduced from Eqs. (V-15) and (V-16) for a series of reaction orders and the $m+10/m$ ratios, where m is the reaction percentage index (ranging from 5 go 85% in steps of 10%) are presented in Table V-2.

The time interval needed to reach a particular fractional conversion can be deduced from the quiet conversion (x)-versus-time (τ) curve. If the initial time is known, any particular time interval can be found by assuming

Table V-2

Conversion Time Ratios for Different Reaction Orders

Reaction order, n	Reaction percentage ratios, τ_m+10/τ_m								
	15/5	25/15	35/25	45/35	55/45	65/55	75/65	85/75	95/85
−5.0	2.351	1.320	1.125	1.052	1.020	1.0007	1.002	1.000	1.000
−4.0	2.549	1.371	1.159	1.074	1.034	1.013	1.004	1.001	1.000
−3.0	2.577	1.430	1.202	1.106	1.056	1.027	1.011	1.003	1.001
−2.0	2.706	1.498	1.255	1.149	1.090	1.053	1.028	1.012	1.003
−1.5	2.774	1.536	1.286	1.176	1.114	1.073	1.044	1.023	1.008
−1.5	2.846	1.577	1.320	1.208	1.143	1.100	1.068	1.043	1.021
−0.8	2.876	1.594	1.335	1.222	1.157	1.113	1.081	1.054	1.029
−0.6	2.906	1.611	1.350	1.236	1.171	1.128	1.095	1.068	1.042
−0.4	2.937	1.629	1.363	1.252	1.187	1.144	1.112	1.086	1.059
−0.2	2.968	1.648	1.383	1.268	1.204	1.162	1.132	1.107	1.084
0.0	3.00	1.667	1.400	1.286	1.222	1.182	1.154	1.133	1.118
0.2	3.032	1.686	1.418	1.304	1.242	1.204	1.779	1.165	1.164
0.4	3.066	1.706	1.437	1.323	1.263	1.228	1.208	1.203	1.228
0.6	3.099	1.727	1.456	1.344	1.286	1.254	1.241	1.249	1.313
0.8	3.134	1.748	1.476	1.365	1.310	1.283	1.279	1.304	1.427
1.0	3.168	1.770	1.497	1.388	1.336	1.315	1.321	1.368	1.579
1.5	3.259	1.828	1.554	1.450	1.408	1.407	1.449	1.582	2.195
2.0	3.353	1.889	1.615	1.519	1.494	1.519	1.615	1.889	3.353
3.0	3.555	2.025	1.757	1.687	1.708	1.819	2.094	2.896	9.184
4.0	3.777	2.181	1.927	1.897	1.991	2.238	2.022	4.687	27.09
5.0	4.021	2.359	2.130	2.157	2.356	2.807	3.885	7.742	81.04

zero time on the concentration-versus-time curve. The reaction order is deduced from a comparison of τ_x with the values tabulated in Table V-2.

If we assume a small value for ε_A, the error in the initial concentration c_{A0}, or for $\varepsilon_{k\tau}$, the error in the dimensionless conversion time $k\tau$, then the difference between the apparent reaction order (found from the table) and the true reaction order $(n'-n)$ will be practically independent of n. Deviations from the true reaction order at $\varepsilon_A = \varepsilon_{k\tau} = \pm 0.1, \pm 0.01, \pm 0.001$ are plotted in Fig. V-3 against the percentage conversion index, m. As is seen,

there is a marked deviation from the true order due to errors in initial time and concentration at initial reaction percentage. The induction, or starting, period for fast reactions may be the source of this error. This effect may be avoided by computing a new reaction index from an arbitrary point on the $c(\tau)$ curve.

Errors in x may be due to an incorrect guess about the stoichiometry, or they may arise from a wrong guess about the dependence of the measured property on concentration. If there is a constant error in the coefficient that relates the measured product concentration to the reactant concentration, the per cent deviation from the true order, $(n-n')\times 100/n$, is equal to the per cent error in the stoichiometric coefficient for the initial (early) reaction percentages ($m \to 0$). For later reaction percentages ($m \to 90$), the deviation rises to a very large magnitude.

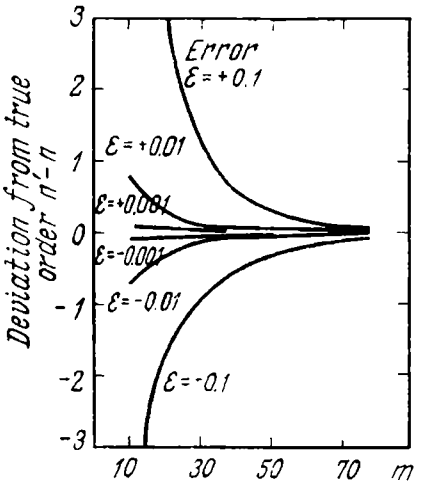


Fig. V-3. Effect of errors in initial time and concentrations on reaction order

An error in the experimentally measured concentration of a reactant which does not contribute to the reaction order leads to the same deviations as are shown in Fig. V-3, except that with increasing positive order the deviations change sign and grow as m tends to 90.

For a great many reactions with a variable n, we may write

$$dx/d\tau = k(1-x)^{\mu}(1-\alpha x)^{\nu} \qquad \text{(V-17)}$$

where k, μ, α and ν may be treated as arbitrary variables. A few examples of such reactions follow:

(1) First-order reversible reactions ($\mu = 0$, $\nu = 1$, $\alpha > 1$).

(2) Simultaneous reactions, one first-order, and the other zero-order ($\mu = 0$, $\nu = 1$, $1 > \alpha > 0$).

(3) Simultaneous reactions, one first-order and the other second-order ($\mu = 1$, $\nu = 1$, $1 > \alpha > 0$).

(4) Many catalytic reactions, including positively catalysed ($\nu > 0$), negatively catalysed ($\nu < 0$), reactant-catalysed ($\alpha > 0$), product-catalysed ($\alpha < 0$).

(5) Reactions in which the reactant contributing to the reaction order is present in a non-stoichiometric concentration.

If a kinetic equation takes the form of Eq. (V-17), the apparent reaction order n' found from Table V-2 will change with m. It has been found that in such a case the function $(n'-\mu)/\nu$ is independent of either μ or ν. A family of curves for a series of values of α on the plot of $(n'-\mu)/\nu$ as a function of m appears in Fig. V-4.

In the general case, when the absolute value is $\nu = 1$, the values of n' and m may be compared with the curve in Fig. V-4 by replacing units of μ on the axis of ordinates. In this way, one can determine α. If the absolute value of ν is other than unity, the points (n', ν) and (m) can be tested for a series of values of ν. The estimates of μ and ν may be used as a check on the fit of the curve to the data.

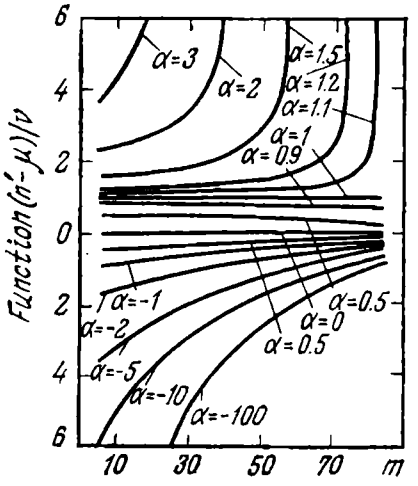


Fig. V-4. Family of curves relating $(n'-\mu)/\nu$ to m

If kinetic experimental data are in the form of the rate of change in concentration as a function of time, one can tabulate time ratios and deduce initial rates for various orders (Table V-3).

In form, such a table is not unlike Table V-2, but knowledge of initial concentrations is unnecessary if we measure the rate of formation of a product whose concentration is proportional to fractional conversion. Then the kinetic equation may be written as

$$dx'/d\tau = k'(1-ax')^n \qquad \text{(V-18)}$$

where x' is the product concentration, k' and a are constants.

Substituting x' from Eq. (V-18) in its integrated form leads to

$$\log_{10}(dx'/d\tau) = -0.4343ak'\tau + \log_{10} k' \qquad n = 1 \qquad \text{(V-19)}$$

$$(dx'/d\tau)^{(1-n)/n} = (n-1)a(k')^{1/n}\tau - (k')^{(1-n)n} \qquad n \neq 1 \qquad \text{(V-20)}$$

Equations (V-19) and (V-20) may directly be applied to rate-versus-time data.

Let the reduced rate w_r be defined as $dx'/d\tau$ divided into the initial rate. Then the time ratio will be

$$\tau_{w_{r2}}/\tau_{w_{r1}} = \log_{10} w_{r2}/\log_{10} w_{r1} \qquad n = 1 \qquad \text{(V-21)}$$

$$\tau_{w_{r2}}/\tau_{w_{r1}} = \frac{w_{r2}^{(1-n)/n} - 1}{w_{r1}^{(1-n)/n} - 1} \qquad n \neq 1 \qquad \text{(V-22)}$$

If the rate is a monotonically decreasing function of time ($n > 0$ and $a > 0$ or $n < 0$ and $a < 0$), then Eqs. (V-21) and (V-22) may be employed to find n. To avoid confusion with the ratios of times needed to reach particular conversions, these new time ratios are called "rate time ratios". Table V-3 should be used exactly as Table V-2 is used.

Table V-3

Rate Time Ratios for Different Reaction Orders

Reaction order, n	Rate time ratio index								
	0.85/0.95	0.75/0.85	0.65/0.75	0.55/0.65	0.45/0.55	0.35/0.45	0.25/0.35	0.15/0.25	0.05/0.15
−4.0	3.402	1.921	1.648	1.558	1.542	1.585	1.715	2.086	4.252
−3.0	3.418	1.932	1.660	1.751	1.558	1.608	1.752	2.159	3.615
−2.0	3.452	1.955	1.683	1.598	1.593	1.656	1.828	2.316	5.455
−1.5	3.486	1.978	1.707	1.627	1.630	1.707	1.910	2.491	6.472
−1.2	3.520	2.001	1.732	1.656	1.668	1.761	1.999	2.684	7.701
−1.0	3.555	2.025	1.757	1.687	1.708	1.819	2.094	2.896	9.184
−0.9	3.579	2.041	1.775	1.708	1.736	1.859	2.161	3.050	10.33
−0.7	3.648	2.089	1.827	1.771	1.820	1.982	2.371	3.546	14.55
−0.5	3.777	2.181	1.927	1.890	1.991	2.238	2.282	4.687	27.09
−0.3	4.107	2.424	2.206	2.257	2.498	3.035	4.033	9.169	116.9
−0.1	5.564	4.558	4.995	6.328	9.103	15.87	40.50	275.6	—
0.1	2.078	1.204	1.059	1.016	1.004	1.001	1.000	1.000	1.000
0.3	2.798	1.549	1.297	1.186	1.123	1.081	1.051	1.029	1.011
0.5	3.000	1.667	1.400	1.286	1.222	1.182	1.154	1.133	1.118
0.7	3.094	1.724	1.453	1.341	1.282	1.250	1.236	1.242	1.299
0.9	3.149	1.758	1.486	1.375	1.321	1.297	1.297	1.331	1.490
1.0	3.168	1.770	1.497	1.388	1.336	1.315	1.321	1.368	1.579
1.2	3.198	1.788	1.516	1.408	1.359	1.343	1.359	1.431	1.741
1.5	3.228	1.808	1.534	1.428	1.383	1.374	1.402	1.502	1.944
2.0	3.259	1.827	1.554	1.450	1.409	1.407	1.449	1.582	2.995
3.0	3.290	1.848	1.574	1.472	1.436	1.442	1.500	1.673	2.505
4.0	3.305	1.858	1.584	1.484	1.449	1.460	1.527	1.722	2.686

V-4. ANALYSIS OF KINETICS AND SELECTIVITY FOR COMPLEX REACTIONS (METHOD OF HYPERBOLAS). CHOICE OF A REACTOR MODEL

Situations sometimes occur with complex reactions where the investigator may lack experimental data, or the reaction mechanism involved may be too complicated, or an early kinetic analysis may be difficult. In such cases, use may be made of the method of hyperbolas described earlier (see p. 301).

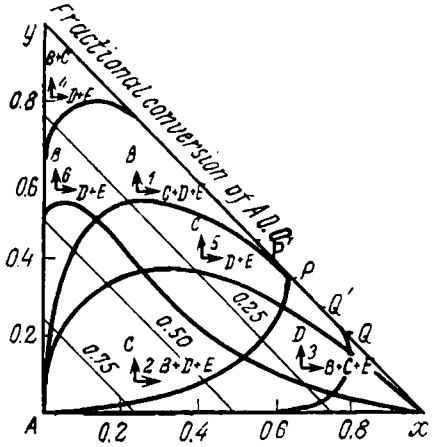


Fig. V-5. Constructing a hyperbola for the reaction $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$

A – 1,1-dichlorethane; *B* – 1,1,1-trichlorethane; *C* – 1,1,1,2-tetrachlorethane; *D* – pentachlorethane; *E* – hexachlorethane

By this method, an analysis is conducted for all reaction components which are classed into three groups: (1) reactants; (2) wanted products; and (3) unwanted products. Experimental data are plotted on a triangular diagram (Fig. V-5), and the line connecting them is a hyperbola described by an equation of the form

$$y = \frac{x(1-x)}{a+bx} \qquad \text{(V-23)}$$

where y is the weight or mole fraction of the reactant turned to a wanted product, x is the weight or mole fraction of the reactant transformed to an unwanted product, a and b are constants.

As an example of the method of hyperbolas, the plot of Fig. V-5 depicts the chlorination of 1,1-dichlorethane to produce hexachlorethane in a continuous stirred tank reactor. The reaction proceeds at 60°C according to the scheme:

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$$

The hyperbolas are obtained by plotting Eq. (V-23). The amount of a wanted product in mole fractions is laid off as ordinate, and the amount of an unwanted product, also in mole fractions, is laid off as abscissa. The lines drawn parallel to the hypothenuze represent the fractional conversion of the reactant. The curves give the selectivity of a given component with respect to other components. For example, curve *1* gives the selectivity of *B* with respect to *C* and *D*. The intersections of the selectivity curves and the fractional conversion lines give the relative selectivity of the reaction components (for example, intersections of curves *1*, *2* and *3* give the relative selectivities for *B*, *C* and *D*) at the respective fractional conversion of *A*.

It should be noted that curves *2*, *3* and *6* in the plot of Fig. V-5 are not hyperbolas, because the components have not been grouped.

Curve *2* intersects the hypothenuze at point *P* on the left of which no reactant *A* has remained unreacted. As the chlorination proceeds, the frac-

tion of C in the reaction products increases, and the experimental points climb the hypothenuze to point P' where C is a maximum; then they go down the hypothenuze. The same is true of curve *3*. At point Q, all of reactant A is converted, while a maximum fractional conversion for D will be at point Q'. In contrast, curve *4* can be approximated by a hyperbola described by Eq. (V-23). The breakdown of B, C and D may be directly obtained from the segments into which curves *1* and *4* divide the fractional conversion lines. Curve *5* giving the selectivity of C with respect to D and E is obtained by grouping B and A, and it can be approximated by a hyperbola.

In order to find the constants a and b in the equation of the hyperbola, $x(1-x)/y-x$ is plotted against x on the basis of experimental data. If the relationship is hyperbolic, the experimental data in such a plot will group in the vicinity of a straight line whose slope is the constant b, and the intercept on the ordinate axis is the constant a (see Example V-1).

At least two or three experiments are needed to evaluate a and b. For example, we may take the reaction time at a low fractional conversion (30%) and at a high fractional conversion (70%); the reference point will then be found at a fractional conversion of about 50%.

Using a triangular diagram and laying off mole fractions of products per mole of reactant, we can obtain curves for each product (see Example V-1). Then for each curve, the values of a and b are found. The lines parallel with the hypothenuze represent the fraction of the reactant remaining unreacted. The intersections of these lines and the hyperbolas define the ratios between all products and the reactant remaining unreacted at a particular stage of the reaction; the respective mole fraction is added to unity.

The y-axis represents the yield of an ith component, $\Phi_i = c_i/c_{A0}$, or $\Phi_j = c_j/c_A$, where $c_j = c_{A0}-c_A-c_i$. Then

$$c_j/c_{A0} = x_A - c_i/c_{A0}$$

The x-axis should preferably represent the fractional conversion x_A of the reactant to the wanted product. The value of x_A at any point on the hyperbola locates a line parallel to the hypothenuze and intersecting the x-axis. On dropping perpendiculars from a point on the hyperbola onto the y- and x-axis and drawing a line parallel to the hypothenuze until it intersects the x-axis, we find that

$$x_A = x+y$$

This also follows directly from

$$y+x = c_i/c_{A0}+c_j/c_{A0} = c_i/c_{A0}+(x_A-c_i/c_{A0}) = x_A$$

The selectivity of an ith reaction component, $\varphi_i = c_i/(c_{A0}-c_A)$, is found by plotting selectivity φ_i against the fractional conversion x_A of reactant A, where $x_A = (c_{A0}-c_A)/c_{A0}$. For this plot, the values of y and x are tabulated as $y+x = x_A$ and $y/(y+x) = \varphi_i$ (see Example V-1).

The shape of the curve in the selectivity-versus-fractional conversion plot gives a clue for the choice of a reactor model that would maximize the yield (see p. 302).

A theory justifying hyperbolic correlation is still lacking. Yet, several authors have successfully applied it to two first-order consecutive reactions of the type $A \rightarrow B \rightarrow C$, and to a combination of two first-order consecutive reactions and a first-order direct-conversion reaction of the type $A \rightarrow C$.

Sometimes, no hyperbolic correlation is reached in plotting curves for any possible combinations of zero, first- and second-order consecutive reactions. This is because the three components A, B, and C are often groups of products rather than individual compounds.

After a hyperbola has been constructed, other variables are varied in order to see whether the hyperbola can adequately fit these additional experimental data. We may construct a hyperbola with a higher maximum and introduce a third parameter leading to

$$y = \frac{x(1-x)}{a+bx+cx^2} \qquad \text{(V-24)}$$

In the method of hyperbolas, special emphasis should be placed on grouping the reaction components. Thus, in a series of consecutive reactions of the type

$$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$$

only the components standing next may be grouped together (see, for example, Table V-4).

Using the method of hyperbolas, we may investigate a great number of catalysts, select the best one, and establish optimum operating conditions for a process, thereby advancing the design of a pilot plant.

In some cases, triangular diagrams may be constructed on the basis of thermodynamic data.

Table V-4

Reaction components	Likely combinations			
	1	2	3	4
Reactants	A	$A+B$	$A+B$	A
Intermediate products	B	$C+D$	C	$B+C$
End products	$C+D+E$	E	$D+E$	$D+E$

Example V-1. Using the method of hyperbolas, reduce data on the chlorination of 1,2-dichlorethane. Experimental data are summarized in Table V-5.

Using the data on the chlorination of 1,2-dichlorethane to 1,1,2-trichlorethane (the wanted product) and 1,1,1,2- and 1,1,2,2-tetrachlorethanes (unwanted products), we construct a plot to evaluate the constants a and b

Table V-5

Data on Chlorination of 1,2-Dichlorethane

Experimental data			Computed data			
y	x	$\frac{x(1-x)}{y}$	x	$y=\frac{x(1-x)}{0.12+0.96}$	$x_A=y+x$	$\varphi=\frac{y}{x_A}$
0.35	0.04	0.11	0.01	0.08	0.09	0.89
0.43	0.11	0.23	0.02	0.14	0.16	0.88
0.45	0.15	0.28	0.05	0.28	0.33	0.85
0.50	0.21	0.33	0.1	0.43	0.53	0.81
0.51	0.28	0.39	0.2	0.51	0.71	0.72
0.52	0.33	0.42	0.3	0.51	0.81	0.63
0.51	0.41	0.47	0.5	0.42	0.92	0.45
—	—	—	0.6	0.34	0.94	0.36
—	—	—	0.7	0.25	0.95	0.27
—	—	—	0.8	0.18	0.98	0.18
—	—	—	0.9	0.09	0.99	0.09

Note. 0.12 = a, 0.96 = b; y is the fraction of 1,2-dichlorethane converted to 1,1,2-trichlorethane, x is the fraction of 1,2-dichlorethane converted to 1,1,1,2- and 1,1,2,2-tetrachlorethanes.

in the equation of the hyperbola (Fig. V-6) and the hyperbola itself (Fig. V-7) described by an equation of the form

$$y = \frac{x(1-x)}{0.12+0.96x}$$

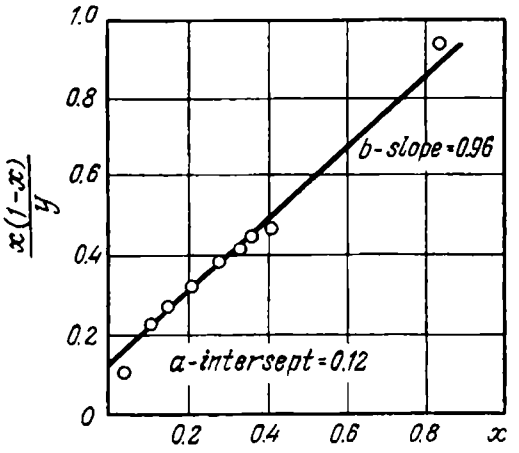


Fig. V-6. Plot to find the constants a and b in the equation of a hyperbola

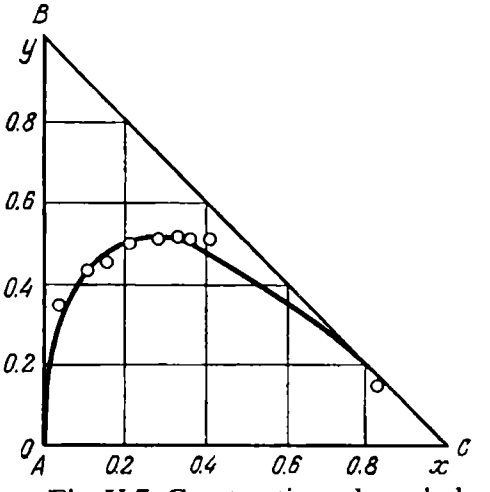


Fig. V-7. Constructing a hyperbola by experimental points

A — 1,2-dichlorethane; B — 1,1,2-trichlorethane; C — 1,1,1,2-tetrachlorethane and 1,1,2,2-tetrachlorethane

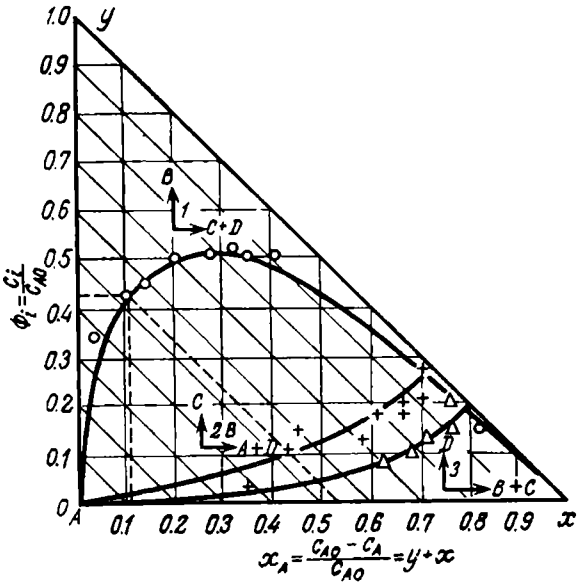


Fig. V-8. Yield as a function of reduced fractional conversion in the chlorination of 1,2-dichlorethane

A — 1,2-dichlorethane; *B* — 1,1,2-trichlorethane; *C* — 1,1,1,2-tetrachlorethane; *D* — 1,1,2,2-tetrachlorethane

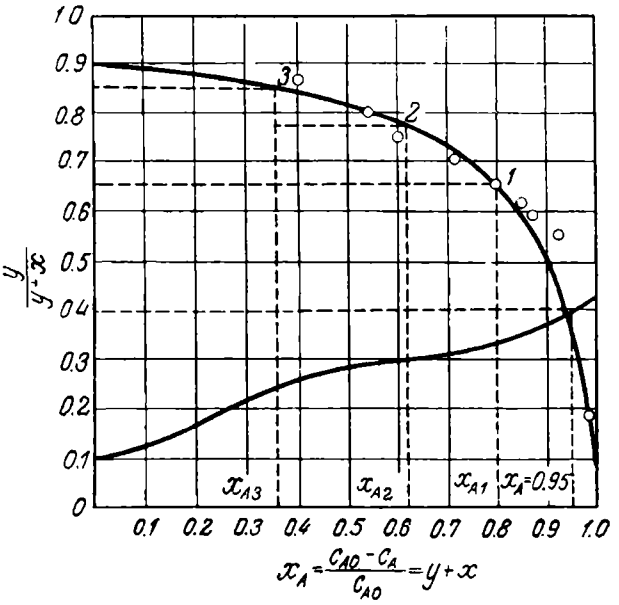


Fig. V-9. Selectivity, φ, as a function of reduced fractional conversion, x_A, in the chlorination of 1,2-dichlorethane

$x_A = 0.95$ — lower curve for a mixture of tetrachlorethanes yield 0.25 (plug flow), yield 0.38 (complete mixing); $x_A = 0.8$ — upper curve for 1,1,2-trichlorethane, yield 0.66 (plug flow), yield 0.52 (complete mixing), yield 0.62 (cascade of three reactors)

Referring to the plot of Fig. V-7, the hyperbola fits the experimental data quite adequately.

By laying off the mole fractions of products per mole of reactant as ordinates, we obtain curves such as shown in Fig. V-8 and described by the equation

$$y = \frac{x(1-x)}{a+bx}$$

where $a = 0.12$ and $b = 0.96$ for curve *1*, $a = 4.5$ and $b = -5.0$ for curve *2*, and $a = 11.0$ and $b = -12.8$ for curve *3*.

A plot of selectivity φ against fractional conversion x_A appears in Fig. V-9. The top curve on which the experimental data are plotted represents the selectivity of 1,1,2-trichlorethane, and the bottom curve gives the selectivity for a mixture of tetrachlorethanes, derived from the plot of Fig. V-8. Referring to Fig. V-9, the yield of 1,1,2-trichlorethane will be a maximum from a plug-flow or a batch reactor (the yield is given by the area under the curve, and at $x_A = 0.8$ it is 0.66), and not from a well-stirred reactor (the yield is given by the area of the rectangle and at $x_A = 0.8$ it is 0.52). With a cascade of reactors for which the rectangles are in the ratio 3:2:1, the yield will be 0.62.

On the other hand, the bottom selectivity curve for a mixture of tetrachlorethanes shows that a well-stirred reactor will give a higher yield than a plug-flow or a batch reactor (at $x_A = 0.95$ the yield from a well-stirred reactor will be 0.38, and that from a plug-flow reactor, 0.25).

V-5. ANALYSIS OF KINETIC DATA BY SEMILOGARITHMIC ANAMORPHISM

The construction of triangular diagrams used in the method of hyperbolas may be avoided in the interpretation of experimental kinetic data by the method of semilogarithmic anamorphism.[4]

Basically, the method consists in that on two kinetic curves plotted at two different temperatures, one finds the residence times corresponding to maxima, and plots them on semilogarithmic coordinates as functions of reciprocal temperature.

If the ratio of the velocity constants of the two reactions remains constant, or if the two reactions have the same or nearly the same activation energies, then the slope of the line connecting the two points will be equal to the ratio of activation energy to the universal gas constant and the intercept on the axis of ordinates will be equal to a dimensionless group comprising the pre-exponential factor, the initial concentration of the reactant, and the constants a and b in the equation of a hyperbola. If, on the other hand, the two reactions differ markedly in activation energies, the rate of one reaction will be negligible in comparison with that of the other, and the complex reaction may be treated as a simple one.

The relationship between the residence time corresponding to a maximum on the kinetic curve and the reciprocal temperature may be described as

$$\ln \theta_m = E/RT + \ln \left[\frac{1}{k_0 + c_{A0}^{n-1}} f(A)\right] \qquad \text{(V-25)}$$

where θ_m is the residence time corresponding to a maximum on the concentration curve, E is the activation energy, R is the universal gas constant, T is the absolute temperature, k_0 is the pre-exponential factor, c_{A0} is the initial concentration of the reactant, n is the reaction order, and $f(A)$ is a function whose form depends on the reaction order, such that

$$A = \frac{1}{b^2}\{(2a+b-ab) + [(2a+b-ab)^2 + (ab-2a-1)b^2]^{1/2}\}$$

For first-order reactions, $f(A) = -\ln(1-A)$. For second-order reactions, $f(A) = A/(1-A)$.

If the values of θ_{m2} and θ_{m1} corresponding to two different temperatures, T_1 and T_2, are known, the energy of activation may be found from an equation similar to that defining the energy of activation for simple reactions

$$E = \frac{RT_1T_2 \ln(\theta_{m2}/\theta_{m1})}{T_1 - T_2} \qquad \text{(IV-26)}$$

The values of θ_{m1} and θ_{m2} may be used to express the relationship between θ_m and T analytically.

A straight line passing through two specified points is described by an equation of the form

$$(y-y_1)/(y_2-y_1) = (x-x_1)/(x_2-x_1)$$

Substituting $\ln \theta_m$ for y and $1/T$ for x in the above equation, we get

$$\ln \theta_m = \frac{T_1T_2 \ln(\theta_{m2}/\theta_{m1})}{T_1 - T_2} \frac{1}{T} + B \qquad \text{(V-27)}$$

where

$$B = \ln \theta_{m1} - \frac{T_2 \ln(\theta_{m2}/\theta_{m1})}{T_1 - T_2}$$

The method of semilogarithmic anamorphism is applicable to consecutive, simultaneous, and consecutive-simultaneous reactions with any functional relationship (not only hyperbolic) between the concentrations of the reaction components.

In simultaneous reactions, there is no maximum on kinetic curves. Therefore, in applying the method of semilogarithmic anamorphism, one should use the dependence of selectivity on residence time at two different temperatures.

Apart from deducing the kinetic constants of complex reactions, the method of semilogarithmic anamorphism is helpful in determining the residence time which maximizes the yield of a wanted product as a function of temperature, that is, in establishing optimum operating conditions for complex reactions.

Example V-2. Using the method of semilogarithmic anamorphism, determine the activation energy for the reaction producing linalyl acetate from linalool and acetic acid and estimate the possibility of cutting down the reaction time. The main reaction proceeds according to the scheme

$$C_{10}H_{18}O + C_4H_6O_3 \rightarrow C_{12}H_{20}O_2 + CH_3COOH$$

The side products of esterification are terpenyl and geranyl acetates. Experimental data are summarized in Table V-6.

Table V-6

Data on Esterification of Linalool

Experiment No.	Temperature, °C	Duration, h	Fractional conversion, %
1	102	42	58.0
2	90	89	58.5

Solution. Using Eq. (V-26) we find that the activation energy for esterification is 16.85 kcal/kg mole.

To determine the reaction time that will give a maximum concentration of the wanted product at other temperatures, use may be made of Eq. (V-27). We may find θ_m for, say, 107.5° and 120°C.

Substituting the values of θ_{m1} and θ_{m2} corresponding to 102° and 90°C in Eq. (V-27), we get

$$\ln \theta_m = 8490/T - 18.9$$

Substituting 107.5° and 120°C in turn in the above equation, we respectively get: $\theta_{m1} = 30.5$ hours and $\theta_{m2} = 15$ hours.

Thus, there is a possibility of cutting down the reaction time.

As a check on whether this cut in reaction time is feasible, two further experiments may be conducted at 107.5° and 120°C. They will show that the actual reaction time securing a maximum concentration of linalyl acetate is 30.0 hours and 15.0 hours, which is in good agreement with the computed values of 30.5 hours and 15.0 hours.

V-6. RATE CONSTANT AS A FUNCTION OF TEMPERATURE

As a rule, the dependence of the rate constant on temperature is expressed as the Arrhenius equation

$$k = k_0 \exp(-E/RT) \qquad \text{(V-28)}$$

where k is the rate constant, k_0 is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the temperature of the reaction.

On taking a logarithm of Eq. (V-28), we get

$$\ln k = \ln k_0 - E/RT \qquad \text{(V-29)}$$

If the condition of Eq. (V-29) is satisfied, then plotting $\ln k$ against $1/T$ will yield a straight line with a slope equal to $-E/R$, which defines the temperature dependence of the rate constant.

V-7. OPTIMUM OBSERVATION TIME SCHEDULE IN KINETIC EXPERIMENTS

As already noted, in any kinetic experiment one determines the concentrations of reaction components and the fractional conversion x as a function of time τ, and calculates the rate of reaction, $dx/d\tau$, for a set of values of τ. This involves m measurements of x at m values of τ. Since τ is measured with sufficient accuracy, all of the error in determining $dx/d\tau$ is attributable to the error in measuring x, the error in x being independent of the value of x. In all but zero-order and autocatalytic reactions, $dx/d\tau$ decreases with increasing fractional conversion. The value of $dx/d\tau$ can be found with the same accuracy for all values of τ only if the sampling times for x are chosen, such that x experience the same amount of change, Δx, over each time interval for the duration of an experiment.

Let the reaction rate be

$$w_r = dx/d\tau \approx \Delta x/\Delta\tau$$

Then the functions $\mu(x)$, $\mu(\tau)$ and $\mu(w_r)$ will be errors in x, τ, and w_r. If $\mu(x)$ is independent of the value of x, and $\mu(\tau) = 0$, then

$$\mu(w_r) = \frac{1}{\Delta\tau}\mu(\Delta x) = \frac{2}{\Delta\tau}\mu(x)$$

and

$$\frac{\mu(w_r)}{w_r} = \frac{2}{\Delta x}\mu(x)$$

Therefore, $\mu(w_r)/w_r$ will remain constant with equal Δx's.

The time schedule that should be followed in determining x so as to obtain the same value of Δx in all measurements may be called an *optimum time schedule*.[5] To develop it, the dimensional variable τ in units of time (say, minutes) is replaced with a dimensionless time, θ. Then, no knowledge of rate constants or the form of the kinetic equation is needed to obtain the time schedule.

With m measurements of x, a set of values is chosen for dimensionless time, $\theta = 0, 1, 2, 3, \ldots, m-1$, and the relationship between θ and τ is defined as

$$\tau = \delta(\Phi\alpha+1)\frac{\theta}{m-1} - \delta \qquad \text{(V-30)}$$

where α and Φ are dimensionless variables, δ is the scale factor equal to $\tau_{m-1}/\Phi\alpha$ (min).

The instant at which kinetic measurements are started is designated as τ_0, the initial time interval as $\tau_1 - \tau_0$, and the overall time interval as $\tau_{m-1} - \tau_0$. At $\tau_0 = 0$, $\tau_1 = \alpha\delta$ and $\tau_{m-1} = \Phi\alpha\delta$, we have

$$(\alpha+1)^{m-1} = \Phi\alpha+1 \qquad \text{(V-31)}$$

where

$$\Phi = \tau_{m-1}/\tau_1$$

On differentiating Eq. (V-30), we get

$$d\theta/d\tau = \frac{m-1}{\delta \ln(\Phi\alpha+1)}(\Phi\alpha+1)^{\theta/(m-1)} \tag{V-32}$$

$$(d\theta/d\tau)_{\theta=0} = \frac{m-1}{\delta \ln(\Phi\alpha+1)} \tag{V-32a}$$

$$(d\theta/d\tau)_{\theta=j} = (d\theta/d\tau)_{\theta=j-1}(\Phi\alpha+1)^{1/(1-m)} \tag{V-32b}$$

The above equations are used as follows. The number m of measurements and the overall time interval τ_{m-1} are specified in advance. On the basis of preliminary experiments, the time τ_1 is found during which the conversion will be a $1/(m-1)$ fraction of the conversion expected at τ_{m-1}, and $\Phi = \tau_{m-1}/\tau_1$ is determined. Using the value of Φ thus found and Eq. (V-31), α is calculated, and using Eq. (V-30), an optimum time schedule is constructed, which gives values of τ for each θ from $\theta = 0$ to $\theta = m-1$. Then Eqs. (V-32) and (V-32*b*) are used to evaluate $d\theta/d\tau$ for each θ. The above computation can readily be performed on a computer.

The use of an optimum time schedule markedly reduces the number of measurements needed. The following values of Φ may be recommended as a rough guide: $2m$ to $2.5m$ for first-order reactions, $7m$ to $9m$ for second-order reactions, of the type $A+A \rightarrow$ products. For second-order reactions of the type $A+B \rightarrow$ products, the top limit of Φ should be anywhere between $5m$ and $7m$ at $[A] = [B]$, and between $3m$ and $5m$ at $[A] > [B]$ or $[B] \gg [A]$.

V-8. CONTROLLING STEPS FOR HETEROGENEOUS REACTIONS

With heterogeneous systems, the first step in kinetic analysis is to identify the controlling step of the process.

Generally, heterogeneous processes may take place in: (a) a kinetic region; (b) a diffusion region and (c) a transition region.

When chemical process proceeds in a *kinetic region*, it is the reaction rate that controls the entire process, while the velocities and physical properties of the streams are of secondary significance.

When a chemical process takes place in a *diffusion region*, the controlling step is the rate at which the reaction components diffuse towards the reaction zone, and which is in turn controlled by the velocities and physical properties of the streams.

When a chemical process takes place in a *transition region*, the rate of chemical change is controlling to the same extent as the rate of diffusion.

In the diffusion region, the reaction rate like the diffusion coefficient, depends but little on temperature and varies with the velocity of the gas stream in the same manner as the Nusselt number, that is, in proportion to the velocity of the gas stream to power 0.4-0.5 in the external diffusion

region, and to power 0.8 under conditions of a turbulent flow in the pore diffusion region.

In the diffusion region, the reaction rate is in no way dependent on the reaction mechanism; different reactions differ in velocity in as much as the reacting species differ in diffusion coefficients and, in the case of reversible reactions, in as much as the conditions of equilibrium are different.

All reactions in the diffusion region are first-order reactions in terms of concentrations of reacting species at constant total pressure. It may be added that the reaction order in terms of total pressure is different from that in terms of concentration.

The conditions favourable for the formation of a diffusion region are high rates of reaction and low rates of diffusion, that is, high temperatures, high pressures and low velocities of the gas stream. Conversely, low temperatures, low pressures and high velocities of the gas stream are conducive to the formation of a kinetic region. The interval between a diffusion and a kinetic region is a transition region where diffusion and kinetics produce a marked effect at the same time.

The fundamental reason why the controlling step may be singled out is that in many cases a complex process is a chain of several consecutive stages. The slowest stage will then be the controlling step of that process.

Several methods may be mentioned for determining which of two regions, diffusion or kinetic, is the controlling step of a process.

(1) Determination from the temperature coefficient of the overall process rate. If a change of 10 °C in temperature causes the overall process rate to change by a factor of two or three (as should be, according to the Arrhenius equation), the controlling step is the chemical change itself. If, on the other hand, a change of 10°C in temperature causes the overall process rate to change by a factor of less than two, the controlling step is mass transfer. In intermediate cases, the reaction proceeds in a diffusion-kinetic region.

(2) Determination on the basis of the apparent reaction order. If the apparent reaction order is other than unity, the controlling step is a chemical change. If, however, the reaction order is unity, the controlling step cannot be pinned down, because mass transfer is a function of concentrations likewise to the first power.

(3) Determination from the relationship between the process rate and the flow pattern. If the process rate is independent of the flow pattern, the controlling step is the chemical change itself. If, on the other hand, the flow pattern affects the process rate, the controlling step is either mass transfer alone or both mass transfer and chemical transformation (which is another way of saying that the reaction proceeds in a diffusion-kinetic region).

The last mentioned method for identifying the controlling step in catalytic-contact reactions may be implemented by one of several techniques.

Technique 1. Two series of experiments are conducted, using two different volumes of catalyst, V_R, in tubes of the same cross-sectional area, with the gas admitted at different molal volumetric rates, V_m, and at a constant gas composition at the inlet. Then the fractional conversion, x, is measured at

the exit at a particular molal feed rate of gas, V_m, and the fractional conversion is plotted against the ratio V_R/V_m (Fig. V-10). If the plot yields a single curve for both series of experiments (Fig. V-10*a*) the kinetic region is controlled, because the process rate is independent of changes in the velocity of the gas phase. If the plot yields a separate curve for each series of experiments (Fig. V-10*b*), the reaction proceeds in the diffusion region. If, finally, the plot yields a single curve at high velocities of the gas flow (that is, at low values of the ratio V_R/V_m), which splits up into two curves at low gas velocities, the kinetic region is controlling in the former case and the diffusion region in the latter (Fig. V-10*c*).

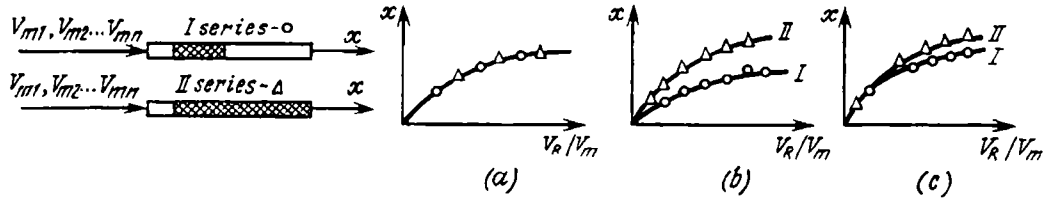


Fig. V-10. Fractional conversion as a function of feed rate and controlling step (first method)
(*a*) kinetic region; (*b*) diffusion region; (*c*) diffusion-kinetic region

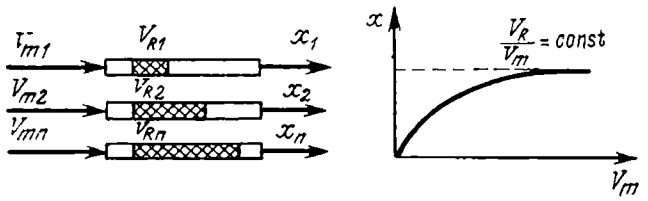


Fig. V-11. Fractional conversion as a function of feed rate and controlling step (second method)

Technique 2. Several experiments are conducted at different molal volumetric rates of gas feed and different volumes of catalyst, but such that the ratio V_R/V_m remains constant. While holding the inlet gas composition the same in all experiments, the fractional conversion is measured. The experimental values of x are then plotted against V_m (Fig. V-11). If x turns out to be fixed, diffusion has no effect on the process, that is, the kinetic region is the controlling step. The curve appearing in Fig. V-11 shows that diffusion affects the process at low gas velocities, while at high gas velocities the process moves into a kinetic region, because the gas velocity affects the process no longer.

The effect of diffusion resistance. In kinetic experiments involving heterogeneous chemical reactions (conducted to establish reaction mechanisms, optimum temperature conditions etc.) it is important that the conditions in a laboratory plant be such that the effect of diffusion resistance is kept to a minimum or, still better, the reaction proceeds completely in a kinetic region. Obviously, it is as important to estimate the extent to which the effect of diffusion resistance has been eliminated and, as a consequence, how accurate experimental data may be.

From the foregoing it follows that the kinetic region should fall within that portion of the $w_r = f(V_m)$ curve where w_r is constant or depends little, if at all, on any further increase in V_m. In the latter case the contribution of diffusion resistance may be evaluated as follows. Equating w_r to the mass transferred through the diffusion layer gives

$$w_r = k_g F_m \Delta P_A \tag{V-33}$$

where w_r is the reaction rate expressed as the moles of component A converted per unit time per unit mass of catalyst, k_g is the coefficient of mass transfer in the gas phase, F_m is the surface area per unit mass of catalyst, and ΔP_A is defined as

$$\Delta P = P_A - P_{Ai}$$

where P_A is the partial pressure of component A in the gas and P_{Ai} is the partial pressure of the same component on the surface of the catalyst.

The coefficient of mass transfer in the gas phase, k_g, enters the generalized equation developed by Chilton and Colburn and modified by Yang and Hougen[6] for heterogeneous reactions

$$j_d = \left(\frac{k_g M_m P}{G}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3} = a\left(\frac{G\sqrt{F_p}}{\mu}\right)^{-n} \tag{V-34}$$

Solving Eqs. (V-33) and (V-34) simultaneously for $\Delta P_A/P_A$ gives

$$\frac{\Delta P_A}{P_A} = \frac{1}{a}\left(\frac{\sqrt{F_p} w_r M_m P}{P_A \mu F_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3}\left(\frac{G\sqrt{F_p}}{\mu}\right)^{n-1} \tag{V-35}$$

In the above equations, P is the total pressure, P_A is the partial pressure of component A, M_m is the average molecular weight of the gas, μ and ρ are the dynamic viscosity and density of the gas, D_{Am} is the average diffusivity of component A in the gas phase, a is a coefficient of proportionality, $G\sqrt{F_p}/\mu$ is the modified Reynolds number Re, F_p is the surface area of a catalyst particle, G is the mass flow rate of the gas. At Re < 620, $a = 2.44$ and $n = 0.51$. At Re > 620, $a = 1.25$ and $n = 0.41$.

On putting

$$X = \left(\frac{\sqrt{F_p} w_r M_m P}{P_A \mu F_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3}$$

and using Eq. (V-35), we then plot $\Delta P_A/P_A$ against X. For a set of values of Re $= G\sqrt{F_p}/\mu$ the plot yields straight lines, radiating from the origin of coordinates at varying angles (Fig. V-12).

On setting the limit of accuracy for the true reaction rate and entering the plot with the applicable ratio $\Delta P_A/P_A$ in the diffusion layer, we find the stream velocities at a given value of the dimensionless group, X. For example, if the reaction rate is to be determined experimentally with an accuracy of 10% or more, diffusion resistance may be neglected if $\Delta P_A/P_A = 0.1$ or less. If the accuracy should be 1%, diffusion resistance may be neglected if $\Delta P_A/P_A = 0.01$ and less, etc.

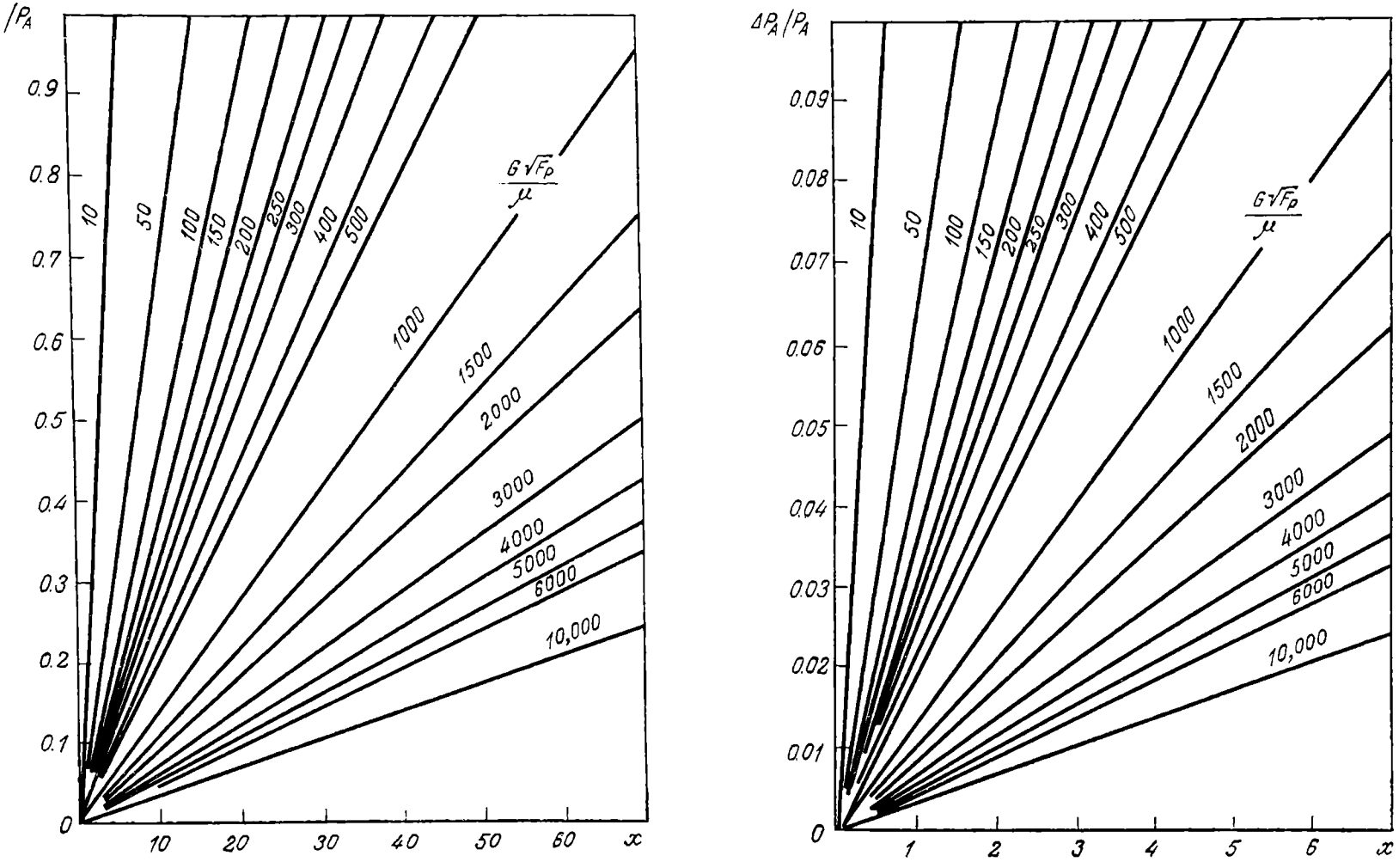


Fig. V-12. Plots to find the controlling step of a process

Diffusion resistance becomes negligible in cases where a reaction proceeds on the surface at a slow rate, and also at high partial pressures of the reacting species.

The following relations may likewise be used as a rough guide in the selection of mass flow rates (the Reynolds number):

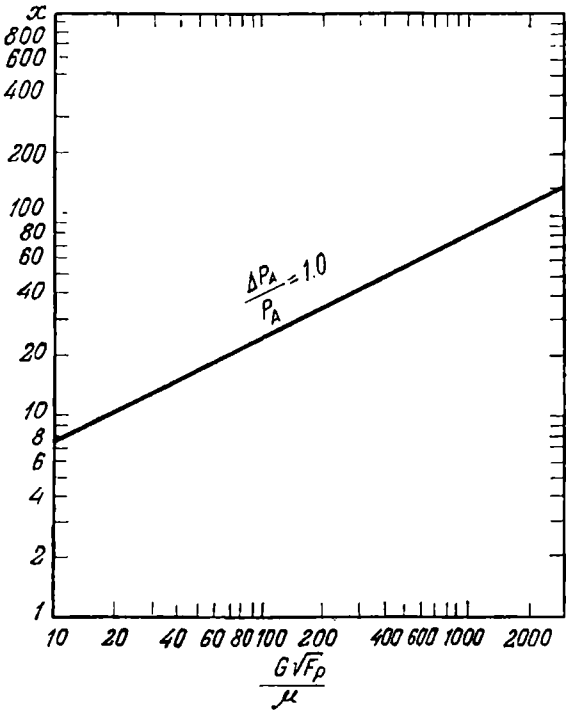


Fig. V-13. Limiting values of X for various values of Re

$\Delta P_A/P_A$	X	$\mathrm{Re} = G\sqrt{F_p}/\mu$
0.1	5	450
0.1	10	17,000
0.01	5	25,000
0.01	10	80,000

Or in words, if the limit accuracy is 10% at $X = 5$, the Reynolds number should be at least 450; at an accuracy of 1% and $X = 5$, the Reynolds number should be at least 25,000.

Diffusion becomes controlling at $P_{Ai} = 0$ and $\Delta P_A/P_A = 1$. This limiting case occurs over an "ideal catalyst", when the surface reaction proceeds instantaneously, and the process is only controlled by the feed rate of reacting species and the rate of product withdrawal. Referring to Fig. V-13, diffusion becomes appreciable, and X cannot take values exceeding those given below at the respective values of Re:

X	300	74	23	7.5
$\mathrm{Re} = G\sqrt{F_p}/\mu$	10,000	1000	100	10

For example, at Re = 100, X cannot exceed 23 (conditions applicable to an ideal catalyst).

V-9. DEDUCTION OF KINETIC PARAMETERS FOR HETEROGENEOUS CATALYTIC REACTIONS

In cases where the overall rate of a heterogeneous catalytic process depends on both kinetics and diffusion, the reaction mechanism and the rate equation are described in terms of the pressures of the reacting species, and resort is made to the concept of adsorption and desorption of reactants and products on active centres (or sites). The rate of a reaction over a catalyst is expressed as the ratio of the product of the kinetic parameter and the driving force

(or the deviation from equilibrium) to the resistance parameter, or

$$\text{Reaction rate} = \frac{\text{(kinetic parameter) (driving force)}}{\text{(resistance parameter)}^n}$$

where the power exponent, n, is usually 1 or 2*.

In order to derive rate equations, experiments are carried out in an integral or a differential reactor under isothermal conditions. With an integral reactor, an experiment is conducted and experimental data are interpreted as follows.

To begin with, observations are made at different pressures or different feed compositions, then the fractional conversion, x, is plotted against the residence time, V_R/V_m. Under isothermal conditions, the plot should yield curves corresponding to the pressures or feed compositions at which the observations were made.

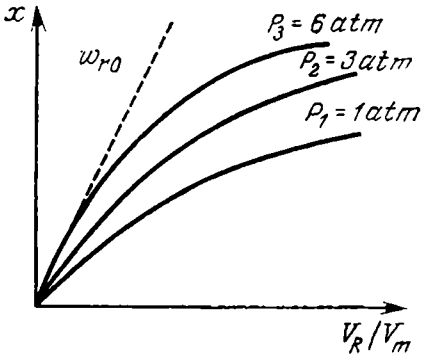


Fig. V-14. Location of experimental observations on $x-(V_R/V_m)$ curves

The experimental curves at $P_1 = 1$ atm (gauge), $P_2 = 3$ atm (gauge) and $P_3 = 6$ atm (gauge) for a reversible reaction of the type $A \rightleftarrows R+S$ are shown in Fig. V-14.

The reaction rate corresponding to a particular value of V_R/V_m can be deduced directly from the plot as the slope of the tangent to the curve at a given point. The slope at $V_R/V_m = 0$ represents the initial reaction rate, w_{r0}, at which reaction products are still non-existent.

(A) FITTING A KINETIC EQUATION TO THE POSTULATED REACTION MECHANISM[7]

As before, let there be a reversible reaction of the type

$$A \rightleftarrows R+S$$

We seek a kinetic equation that will fit the postulated reaction mechanism best. This can be done in one of several ways.

Method 1. It is assumed that a linear relationship exists between the reaction rate, on the one hand, and the kinetic constants and pressures, on the other. This relationship can be approximated by a straight line

$$f(w_r) = a+bP_A+cP_R+dP_S \qquad \text{(V-36)}$$

We further assume that the kinetic equation may be written as

$$w_r = \frac{k(P_A - P_R P_S/K)}{1+k_A P_A+k_R P_R+k_S P_S}$$

* Different hypotheses of reaction mechanisms lead to a variety of forms of kinetic equations. One of such widely used forms is the exponential relation (see G. Boreskov. All-Union Conference on Chemical Reactors, vol. IV. Novosibirsk, 1966).

or as

$$w_r = \frac{(P_A - P_R P_S/K)}{a + bP_A + cP_R + dP_S}$$

The last equation may be re-cast as follows

$$\frac{P_A - P_R P_S/K}{w_r} = a + bP_A + cP_R + dP_S \qquad \text{(V-37)}$$

In Eq. (V-37) the constants of the kinetic equation are in linear form, and the left-hand side is a function of the reaction rate.

Suppose that the equilibrium constant K is known. If it is not known, it may be deduced from the previous plots of x versus V_R/V_m, because in approaching a state of equilibrium the fractional conversion tends asymptotically to a constant value. The reaction rate w_r and the respective partial pressures may likewise be deduced from the x-*vs*-V_R/V_m curves.

The constants are estimated by the method of least squares. Should any constant be negative, the postulated reaction mechanism must be revised.

It should be remembered that the above method is only applicable to cases where P_A, P_R and P_S are independent variables. Therefore, the x-*vs* -V_R/V_m curves should be plotted for experiments in which the initial mixture contains not only component A, but also R or S or both; otherwise, P_R and P_S will not be independent variables.

Method 2. The shape of the curve $f(w_r)$ is analysed in relation to the pressure P_A of the reactant A. For any reaction mechanism that may exist, the rate equation can be written as

$$f(w_r) = a' + b'P_A \qquad \text{(V-38)}$$

Then $f(w_r)$ is plotted against P_A. If the plot yields a straight line, the rate equation fits the assumed reaction mechanism.

Suppose that the rate equation has the form

$$w_r = \frac{k(P_A - P_R P_S/K)}{1 + k_A P_A + k_R P_R} \qquad \text{(V-39)}$$

or

$$\frac{P_A - P_R P_S/K}{w_r} = a + bP_A + cP_R \qquad \text{(V-40)}$$

For experiments using a pure reactant, A, as the feed, the following relationship will hold

$$P = P_A + P_R + P_S$$
$$P_S = P_R$$
$$P_R + P_S = 2P_R$$
$$P_R = \frac{P - P_A}{2}$$

Then Eq. (V-40) may be re-written as

$$\frac{P_A - (P_R - P_S)/K}{w_r} = a' + b'P_A$$

where $a' = a + 1/2\ cP$ and $b' = b - 1/2\ C$.

Now $[P_A-(P_R-P_S)/K]/w_r$ is plotted against P_A for a set of values of total pressure (Fig. V-15). The plot yields parallel lines. In order to find the values of a and b, the intersections should be plotted against the total pressure P. The slope of a straight line in this plot will give $1/2c$, and the intercept on the axis of ordinates will give the value of a. The constant, b, can be deduced from the slope of the straight lines in Fig. V-15 and the value of c.

Method 3. The constants of kinetic equations are fitted by an iterative procedure on a computer. Using the data obtained by the previous methods, the constants of the kinetic equations can be conveniently verified on a computer (see p. 87), thereby providing a test of fit for the kinetic equation. With a computer, the amount of experimentation needed is markedly reduced, because experimental data are only used for a check on those computed, provided the experiment has been appropriately designed and executed.

Method 4. Deductions may be made from the initial rates of reactions. The initial or equilibrium states (in the case of reversible reactions) of the system in question are readily definable to a sufficient degree of accuracy. Therefore, the initial reaction rates may be used in testing the nominated reaction mechanism for plausibility and the respective kinetic equation for adequacy. Then, taking the dependence of the initial rates on pressure and feed composition as a guide, the reaction kinetic may be finalized, using one of the above methods.

The initial reaction rate can be deduced from x versus V_R/V_m plots, in any one of four ways:

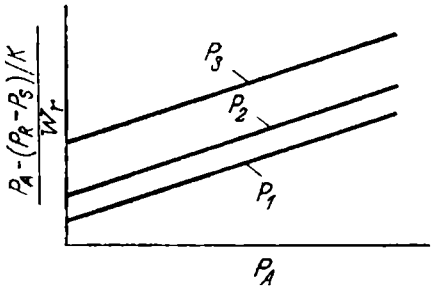


Fig. V-15. To determining the form of a kinetic equation

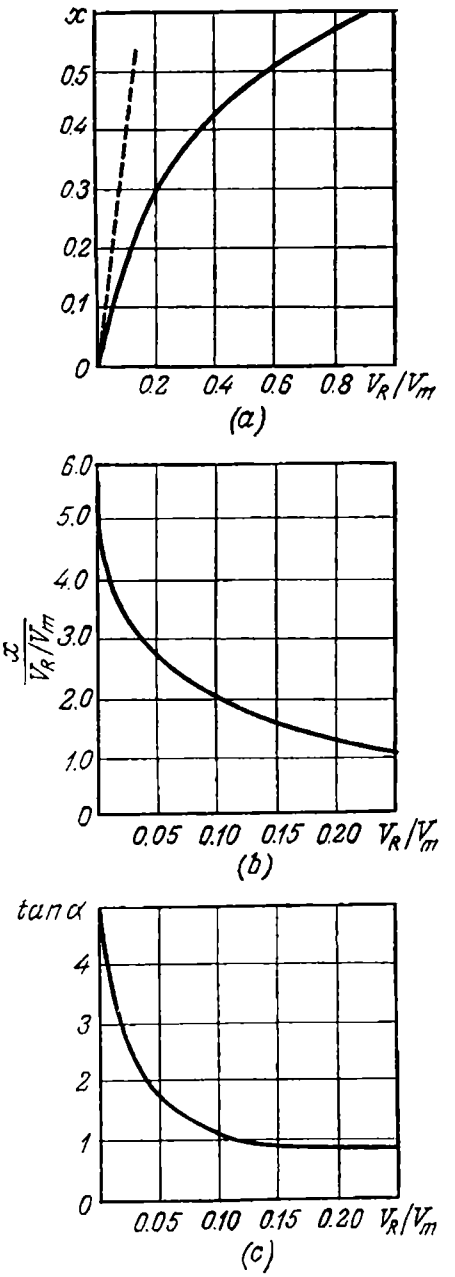


Fig. V-16. Determining the initial rates of reactions

(1) Using the plot of x against V_R/V_m of Fig. V-16*a*, the slope of the curve is found at $x = 0$;

(2) A plot of $x/V_R V_m$ against V_R/V_m is constructed, and extrapolation is made to $V_R/V_m = 0$ (Fig. V-16*b*);

(3) The slope of the x-versus-V_R/V_m curve is measured at several points, the values thus obtained are plotted as $\tan\alpha$ against V_R/V_m, and the curve is extrapolated to $V_R/V_m = 0$ (Fig. V-16*c*).

(4) An empirical equation describing the experimental plot of x against V_R/V_m is fitted and differentiated.

The first method gives the initial reaction rate directly, but it suffers from a major drawback in that the accuracy of experimental data is insufficient at the beginning of the x-versus-V_R/V_m curve.

The second method is advantageous in that it makes unnecessary knowledge of the slope, but at $V_R/V_m = 0$ the ordinate on the plot of $x/(V_R/V_m)$ -versus-V_R/V_m may lie above that given by interpolation.

The third method requires an accurate knowledge of the slope, but it uses the terminal values of V_R/V_m which give more accurate values of $\tan\alpha$.

With the fourth method, it is not always possible to fit an equation.

The choice of a particular method depends on the nature of the reaction under study and the course of the x-versus-V_R/V_m curve.

The effect of changes in pressure on the initial reaction rate. Of all factors affecting the kinetics of heterogeneous gas-solid reactions, pressure is most important. Consider four types of reactions:[6]

$$\text{(I) } A \rightleftarrows R;\ \text{(II) } A \rightleftarrows R+S;\ \text{(III) } A+B \rightleftarrows R;\ \text{(IV) } A+B \rightleftarrows R+S$$

In the above reactions, the rates may be controlled by any one of the following mechanisms.

(A) A reaction takes place between the adsorbed molecules of reactants and products in the presence (or absence) of the dissociation of any adsorbed component. Under the circumstances, any one of the following steps may be controlling: (a) adsorption of component A; (b) adsorption of B; (c) desorption of R; (d) a surface reaction.

(B) A reaction takes place between the adsorbed atoms of A; B, R and S are adsorbed as molecules. After dissociation, A is adsorbed on adjacent active centres. Under the circumstances, any one of the following steps may be controlling: (e) adsorption (and dissociation) of component A; (f) adsorption of B; (g) desorption of R (or S); (h) a surface reaction.

(C) Reactant B is not adsorbed. Molecules of A, R and S are adsorbed. Under the circumstances, any one of the following steps may be controlling: (i) adsorption of A; (j) desorption of R; (k) a surface reaction.

(D) Reactant B is not adsorbed. Atoms of A and molecules of R and S are adsorbed. After dissociation, A is adsorbed on adjacent active centres. Under the circumstances, the controlling step may be: (l) adsorption of A; (m) desorption of R; (n) a surface reaction.

(E) Reactant A is not adsorbed. Molecules of B, R and S are adsorbed,

the controlling step being as follows: (o) collisions of molecules of A; (p) desorption of R (or S); (q) adsorption of B.

(F) An uncatalysed reaction takes place. Here, the controlling step may be (r) a homogeneous gas-phase reaction.

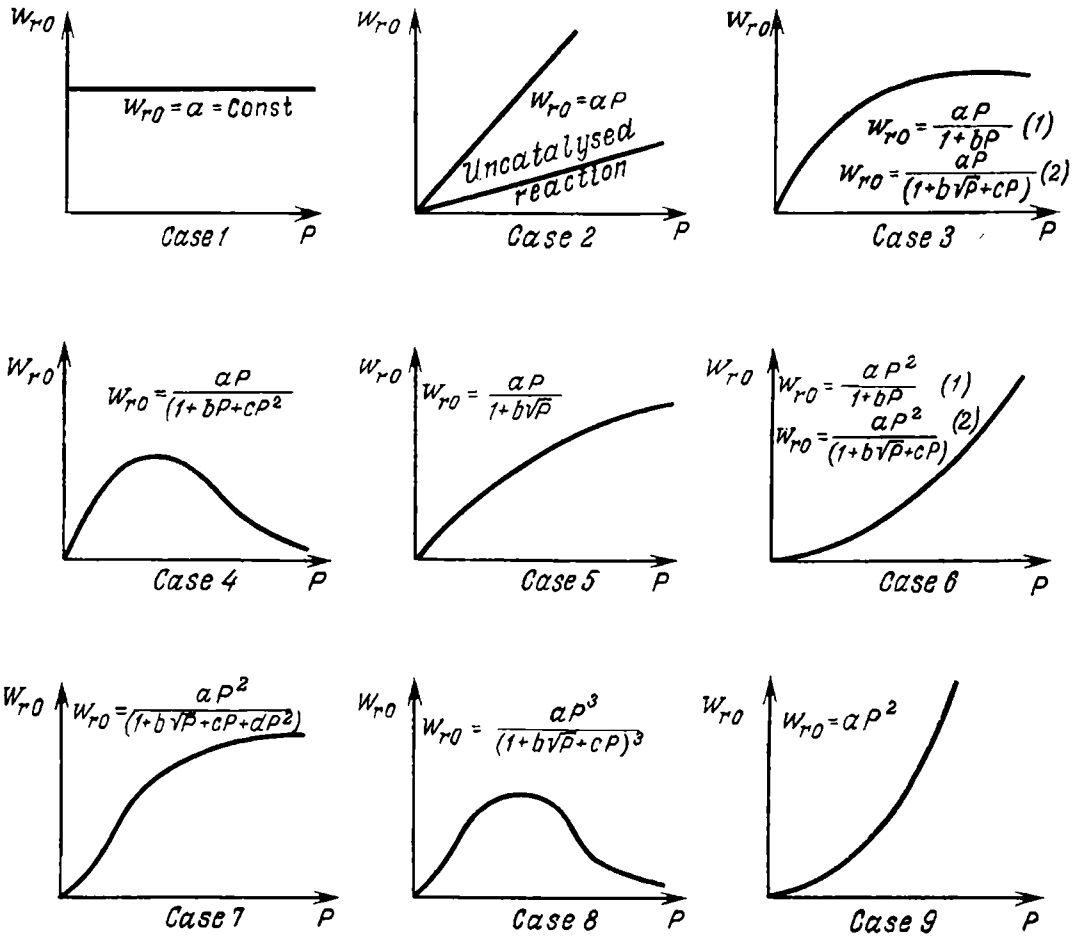


Fig. V-17. Initial rates of simple gas-phase reactions. Effect of total pressure

The design equations and plots for determining the initial rates and mechanisms of the above reactions are given in Fig. V-17. In these plots, the initial reaction rate, w_{r0}, is laid off as ordinate and the total system pressure, P, as abscissa. On the basis of Fig. V-17, Tables V-6*a* through V-15 define the controlling steps for nine major cases that may be encountered in practice.

Case 1. The catalyst is poisoned in the course of the reaction. One of the products is desorbed; $K = \infty$ (Table V-6*a*).

At $K_e \neq \infty$ (an equilibrium adsorption of S), the controlling steps of the process are found from Table V-7.

Case 2. The initial reaction rate increases linearly with rising total pressure. The same is true of uncatalysed reversible reactions. One of the re-

Table V-6a

Reaction type			
I	II	III	IV
Mechanism			
c	*c*	*c*	*c*
g	*g*	*g*	*g*
j	*j*	*j*	*j*
m	*m*	*m*	*m*
—	—	*p*	*p*

Table V-7

Reaction type			
I	II	III	IV
Mechanism			
—	*c*	—	*c*
—	*g*	—	*g*
—	*j*	—	*j*
	m	—	*m*
—	—	—	*p*

actants is adsorbed (or other reactants are not adsorbed or not present). The reaction is uncatalysed (Table V-8).

Table V-8

Reaction type			
I	II	III	IV
Mechanism			
a	*a*	—	—
e	*e*	—	—
i	*i*	*i*	*i*
l	*l*	*l*	*l*
—	—	*g*	*g*

Case 3. The initial reaction rate asymptotically tends to a maximum value. The controlling step is the adsorption of $A(A+B \rightleftarrows)$. The controlling step is the adsorption of $B(A+B \rightleftarrows)$. There is a surface reaction $(A \rightleftarrows R)$.

The reaction takes place on the surface ($2A \rightleftarrows$). One of the products is desorbed; $K \neq \infty$ (Table V-9).

Table V-9

Reaction type			
I	II	III	IV
Mechanism			
c ($K \neq \infty$)	—	a	b
d	—	a	b
g ($K \neq \infty$)	—	—	—
h	h	—	—
j ($K \neq \infty$)	—	—	—
k	—	—	—
m ($K \neq \infty$)	—	—	—
n	—	—	—

Case 4. The initial reaction rate has a nearly linear initial portion, passes through a maximum, and asymptotically decreases at high pressures. The controlling step is a surface reaction ($A \rightleftarrows R+S$). Adsorption of A is controlled by dissociation ($A+B \rightleftarrows R+S$). The reaction mechanism can be found from Table V-10.

Table V-10

Reaction type			
I	II	III	IV
Mechanism			
—	d	—	—
—	—	e	e
—	k	—	—

Case 5. The initial reaction rate progressively rises with pressure, starting with a linear change, and approaches a value proportional to the square root of pressure. Adsorption of B is controlled by dissociation of A($A+B \rightleftarrows$). The reaction mechanism can be found from Table V-11.

Table V-11

Reaction type			
I	II	III	IV
Mechanism			
	—	j	j
	—	—	—

Case 6. At low pressures the reaction rate rises in proportion to the square of pressure and approaches a value proportional to pressure to the first power. The controlling step is a surface reaction, B is not adsorbed ($A+B \rightleftarrows \rightleftarrows R$). The controlling steps are collisions, A is not adsorbed ($A+B \rightleftarrows R$). The controlling step is a surface reaction, A is dissociated, B is not adsorbed ($A+B \rightleftarrows$). The reaction mechanism can be found from Table V-12.

Table V-12

Reaction type			
I	II	III	IV
Mechanism			
–	–	k	—
—	—	o	
—	—	n	n

Case 7. At low pressures the reaction rate rises in proportion to the square of pressure, then asymptotically tends to a constant value. The controlling step is a surface reaction; there is no dissociation ($A+B \rightleftarrows$); same (B is not adsorbed). The controlling steps are collisions of $A(A+B \rightleftarrows R+S)$. The controlling step is the desorption of one of the products ($A+B \rightleftarrows R$): $K \neq \infty$ (Table V-13).

Table V-13

Reaction type			
I	II	III	IV
Mechanism			
—	—	$c\ (K \neq \infty)$	—
—	—	d	d
—	—	$g\ (K \neq \infty)$	—
—	—	$j\ (K \neq \infty)$	k
—	—	m	o
—	—	$p\ (K \neq \infty)$	—
—	—	p	—

Case 8. At low pressures the reaction rate rises with the square of pressure, passes through a maximum, and falls off at high pressures. A surface reaction is controlled by dissociation of $A(A+B \rightleftarrows)$. The reaction mechanism can be found from Table V-14.

Table V-14

Reaction type			
I	II	III	IV
Mechanism			
-	—	*h*	*h*
—	—	—	—

Case 9. The initial reaction rate rises with the square of pressure. The controlling step is an uncatalysed reaction ($A+B \rightleftarrows$). The reaction mechanism can be found from Table V-15.

Table V-15

Reaction type			
I	II	III	IV
Mechanism			
—	—	*r*	*r*
—	—	—	—

The plots of Fig. V-18 illustrate six typical relationships between the initial rates of bimolecular gas-phase reactions and the feed composition per mole fraction of component $A(N_A)$. Comments on these six cases are given below.

Case 1. The controlling step is the rate of adsorption of A (component B is not adsorbed).

According to the classification given earlier (see p. 392), the mechanism that applies may be *i* and *l*. The initial reaction rate rises linearly with the mole fraction of reactant A. Extrapolation of the straight line to $N_A = 1.0$ points to an increasing rate of adsorption of A in the absence of B. However, the catalyst is saturated with A rapidly, and the reaction ceases.

Case 2. The controlling step is the rate of adsorption of B, if A is not adsorbed. The mechanism that applies is *q*. Extrapolation to $N_A = 0$ gives a maximum value corresponding to the rate of adsorption of B in the absence of A.

Case 3. The controlling step is the rate of adsorption of A accompanied (or not) by the dissociation of A, while component B approaches a state of equilibrium adsorption. Mechanisms *a* and *e* apply. The initial reaction rate rises faster than linearly.

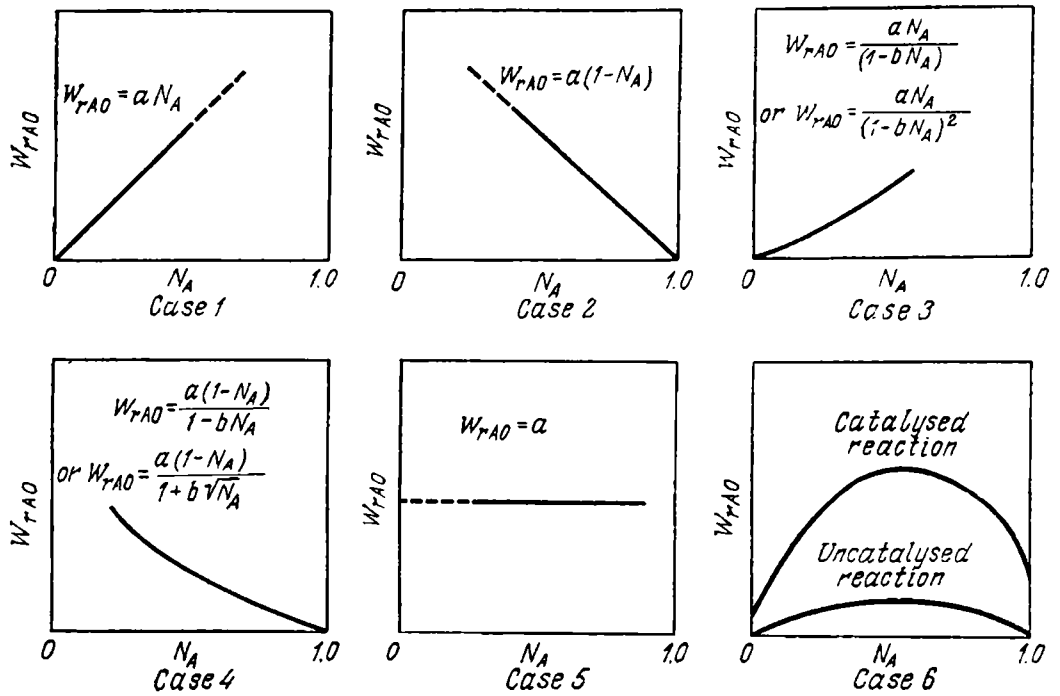


Fig. V-18. Initial rates of bimolecular gas-phase reactions. Effect of the initial composition, N_A

Case 4. The controlling step is the rate of adsorption of B, accompanied (or not) by the dissociation of A and with A approaching an equilibrium adsorption. Mechanisms *b* and *f* apply.

Case 5. The initial reaction rate is independent of the feed composition. The controlling step is the rate of desorption of R at $K = \infty$ for reactions of the type $A+B \rightleftarrows R$. Mechanisms *c*, *g*, *j*, *m* and *p* apply. In situations where the controlling step is the rate of desorption of R and $K \neq \infty$ for reactions of the type $A+B \rightleftarrows R+S$, mechanisms *c*, *g*, *j*, *m* and *p* apply.

Case 6. The controlling step is the rate of the reaction on the surface of the catalyst. Mechanisms *d*, *h*, *k*, *n* and *o* apply. As an alternative, the controlling step may be the rate of desorption ($K \neq \infty$) for reactions of the type $A+B \rightleftarrows \rightleftarrows R$, to which mechanisms *c*, *g*, *j*, *m* and *p* apply. This case is also typical of uncatalysed reactions proceeding by mechanism *r*.

If the initial reaction rate is zero in the presence or absence of component A or B and passes through a maximum close to the average component concentrations, the equations presented in Table V-16 apply.

(B) FINAL TEST OF THE KINETIC EQUATION

After a kinetic equation has been fitted, it is tested as follows:

(1) The reaction rate w_r, is found for a set of values of x.
(2) The space time V_R/V_m is found for a series of values of x.
(3) The reciprocal of reaction rate, $1/w_r$, is plotted against x (Fig. V-19).

Table V-16

Equation of initial rate	Reaction type and mechanism
$w_{r0} = \frac{aN_A(1-N_A)}{1 \pm bN_A - cN_A^2}$	(III) *c*, *p*, *j* ($K \neq \infty$)
$w_{r0} = \frac{aN_A(1-N_A)}{a+b\sqrt{N_A}+cN_A-N_A^2}$	(III) *q*, *m* ($K \neq \infty$)
$w_{r0} = \frac{aN_A(1-N_A)}{(1+b\sqrt{N_A-cN_A})^2}$	(III) *h*; (IV) *h*
$w_{r0} = \frac{aN_A(1-N_A)}{(1+b\sqrt{N_A})^2}$	(III) *n*; (IV) *n*
$w_{r0} = \frac{aN_A(1-N_A)}{(1 \pm bN_A)^2}$	(III) *d*; (IV) *d*
$w_{r0} = \frac{aN_A(1-N_A)}{1 \pm bN_A}$	(III) *k*, *o*; (IV) *k*, *o*
$w_{r0} = aN_A(1-N_A)$	(III) *r*; (IV) *r*

(4) The area under the curve is found for a set of consecutive values of x, noting that

$$V_R/V_m = \int_0^x dx/w_r$$

(5) The values found by integration and from the V_R/V_m-versus-x curve are compared. The data plotted include both the experimental data used in deriving the equation, and the data that have not been interpreted.

(6) Since the constants of kinetic equations are temperature-dependent, they must be determined at several temperatures. Correlation can conveniently be obtained on the $\log_{10} K$-versus-$1/T$ coordinates (Fig. V-20). For each constant, the resultant equation is of the form

$$\log_{10} K = a/T + b$$

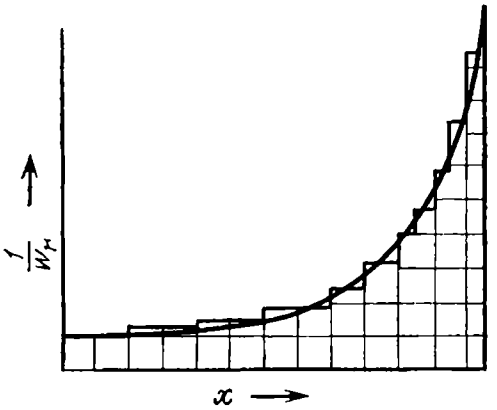


Fig. V-19. Reciprocal reaction rate, $1/w_r$, as a function of fractional conversion, x

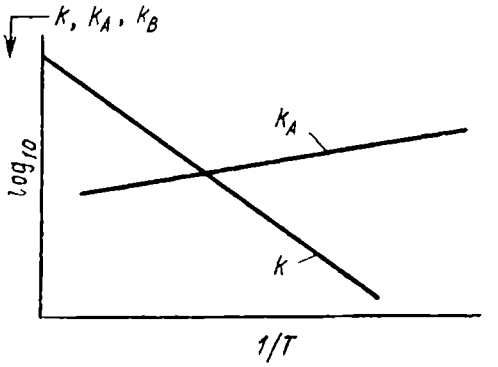


Fig. V-20. Plot of $\log_{10} k$ as a function of $1/T$

(7) Sometimes equilibrium adsorption constants may be deduced by independent methods.[8] In such cases, there must be a fair degree of agreement with the values obtained.

Some procedural hints. Kinetic experimentation in differentia land integral reactors under isothermal conditions is relatively simple to carry out. However, the results lack in accuracy, especially at high heats of reaction, high activation energies, considerable radial gradients, etc. Under the circumstances, any one of the following techniques may be used to advantage:

(1) *The steady-state recycle technique*, when the pump installed in the recycle circuit returns the stream emerging from the isothermal layer with an addition of fresh feed in proportion to the amount withdrawn from the system upon chemical change.[8,9]

(2) *The unsteady-state recycle technique*, when changes in concentration with time are measured while maintaining a continuous recycle through the isothermal layer.

(3) *The turbulizing-generator technique*, when the gas passing over a catalyst is maintained at a high flow rate by a reciprocating plunger with an addition of small amount of fresh feed and product withdrawal.[10]

(4) *The adiabatic-reactor method*, when a steady-state longitudinal temperature or constant profile is measured in a multi-stage stationary-stream vertical reactor. The reaction rates are deduced from the resultant profiles by graphical differentiation.[11]

We shall take up the recycle methods in greater detail because they are most widely used.

Recycle methods. In sketch form, a recycle plant is shown in Fig. V-21. The system is brought up to conditions characteristic of the steady state. Then the reaction rate will be the same at all points within the catalyst bed in each experiment. In other words, the bed will operate under conditions of complete mixing. With no recycle ($x_{Ai} = x_{A0}$), we have

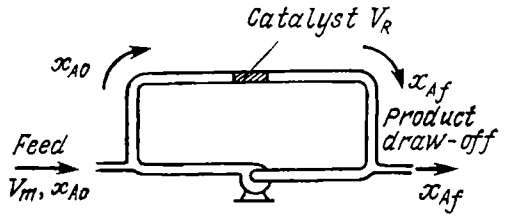


Fig. V-21. Sketch of a recycle plant

$$(-w_{rA})_{av} = \frac{x_{Af} - x_{A0}}{V_R/V_m} \qquad \text{(V-41)}$$

where $(-w_{rA})_{av}$ is measured at some average fractional conversion of the streams entering and leaving the catalyst bed.

Thus,

$$x_{Af} > x_{A\,av} > x_{A1} \qquad \text{(V-42)}$$

Since the difference $x_{Af} - x_{Ai}$ may be appreciable, an improper choice of fractional conversion in deducing the average rate of reaction may entail a considerable error.

Now we assume that some of the product is recycled. With an increase in recycle flow rate, the fresh feed is mixed with an increased amount of

product, thereby causing x_{Ai} to approach x_{Af}. From Eq. (V-42) it follows that the assumption of a constant rate does not hold. In other words, with a high rate of recycle we get

$$(-w_{Ar})_f = \frac{x_{Af} - x_{A0}}{V_R/V_m} \tag{V-43}$$

where $(-w_{Ar})_f$ is deduced from the conditions in the exit stream or is based on changes in the fitted catalyst volume, V_R or V_m.

Among the advantages offered by the recycle method are:

(1) The rate of reaction is directly measured in each experiment.

(2) Significant changes in reactant concentration are propagated throughout the system, and the effect of errors in the analysis of the feed and product streams is thus minimized, thereby enhancing the accuracy of rate measurements.

(3) The heat of reaction has a smaller effect, and the temperature can therefore be controlled to closer tolerances.

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CHAPTER VI

MACROKINETICS EXPERIMENTS AND INTERPRETATION OF PILOT-PLANT KINETIC DATA

VI-1. GENERAL

Pilot-plant experiments are an important step in the investigation of a process towards formulating specifications for a commercial plant.

A pilot plant uses the microkinetic data derived by laboratory experimentation and yields information about the macrokinetics of a process, that is, about the interaction of large conglomerates of molecule, macroscopic fluid elements, the effect of the macroscopic streams of materials and energy on the process, and also the true residence time in a real apparatus.

The key objectives of studies into the macrokinetics of a process are to estimate the coefficients of a mathematical model of the process and to test the model for adequacy. This is why the investigator usually operates as part of a man-computer loop, with the computer providing a means for adequacy tests of models.

The functions of a pilot plant (to be taken up later in greater detail) are:

(1) To identify the flow pattern of the prototype system by subjecting it to a step, impulse or sinusoidal disturbance (by injection of a tracer material). As a result, the system is classed as one of complete mixing or plug flow, and the choice is made between a dispersion, cascade or hybrid model.

(2) The effect of thermal parameters is investigated, a more accurate estimate of conditions under which heat transfer takes place and a more accurate value of the heat transfer surface area are found; the process is investigated for thermal stability.

(3) A more accurate estimate of the effects produced by diffusion parameters is made and the process is arranged to proceed in a kinetic or a diffusion region. Then the reactor efficiency is determined on the basis of the model chosen (see p. 292).

(4) The system is investigated under dynamic conditions, with disturbances acting over various circuits and with process variables changing in time, and recommendations are made as regards the control of the system.

(5) A complete mathematical model of the system is developed, which is then tested and fitted to the system with the aid of a computer.

(6) The mathematical model is optimized, the optimal conditions are reproduced, and the necessary improvements are made.

Before commencing a large-scale experimentation on the system of interest, at least an approximate idea must be formed about the mathematical model that might fit the system.

Firstly, it is important to decide which process variables will be changed and which held constant in the course of the experiment, that is, which variables will be dependent and which independent. An optimization criterion must likewise be selected.

Secondly, the order of magnitude of the quantities to be measured should be determined, at least approximately.

Thirdly, the variables must be ranked according to their effects, and a measure (or weights) of their effects must be established.

Fourthly, the relationships that might exist between the variables must be ascertained. A rough check is made on the form of the relationship $y = f(x_1, x_2, \ldots, x_r)$ to see whether it is linear or nonlinear. A test for a power relationship can be carried out on logarithmic paper, etc.

Recalling the concepts of statistics, any observation is a *random variable*. Associated with each random variable are its *expected value* and its *deviation* from the expected value, which is a stochastic or random entity like the variable itself.

A deviation from the expected value is thus a *random error*. Random errors can be conveniently processed; once their magnitudes are known, it is an easy matter to define confidence intervals for them, or to reduce them by increasing the sample size as appropriate.

Errors introduced continuously and due to, say, faulty calibration of an instrument or to a preconceived idea of the expected data are called *systematic errors*. Systematic errors are much more difficult to trace because nothing is known about their presence; yet, the matters of calibration should always be taken up as "suspicious".

Several methods exist for eliminating or minimizing systematic errors. Some of them are outlined below.

(1) The sample is tested to see whether it is representative. It may prove fruitful to use the statistical methods described earlier (see Chap. II). By these methods, the various factors are ranked according to their effect on the process under study, and those carrying more "weight" are retained.

(2) The observer's bias is eliminated. An experienced observer will arrange the experiment so that his own preconceived ideas would not affect the result. In contrast, an inexperienced investigator is likely to rely upon his judgement always.

(3)Absolute measurements should be replaced with relative ones wherever possible. This requirement may be reduced to an accurate calibration of the instruments.

(4) The range of study is modified and extended

(5) The effect of unknown variables is eliminated by carrying out "control" experiments.

It is typical of some batch chemical processes that their variables change continually and monotonically with time between an upper and a lower limit. Examples are the decrease in moisture content or the increase in dry matter in the operation of drying, the increase in the weight fraction of particles having a specified size in the operation of comminution, etc.

A similar situation occurs during transients in the case of stationary processes, such as changes in gas (vapour) to liquid ratios in absorption and rectification, or changes in the temperature of a heat-transfer medium in heat-exchange processes.

Most often, the above processes are adequately described by linear differential equations of various orders. For practical purposes, however, they may be approximated by first-order equations. This corresponds to unsteady-state processes described by equations of the form

$$Y(t) = Y_m[1-\exp(-\tau/T)] \qquad \text{(VI-1)}$$

where Y_m is the maximum value of Y, T is the time constant, and τ is the current time.

Y_m is found as a peak on the experimental transient response, and T is the projection of the tangent to the curve on the axis of abscissae between the point of tangency and the straight line $Y = Y_m$. So that Y_m and T can be deduced as explained, the transient response must be plotted over a time interval of at least $3T$.

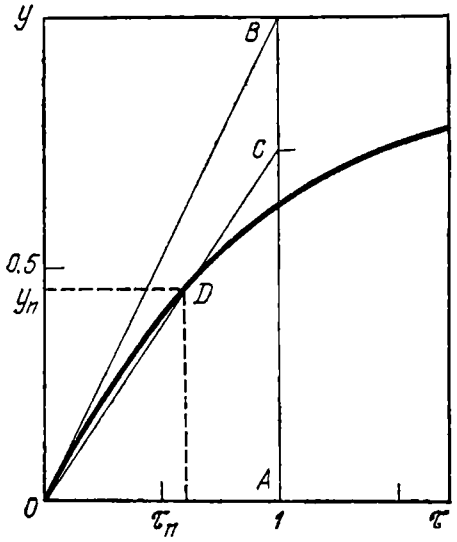

Fig. VI-1. An example of graphical determination of τ_i and Y_i from an experimental transient response, ($AC/AB = {}^3/_4$)

By another method (explained below),[1] Y_m and T can be determined, using only the initial portion of the transient response (between $0.5T$ and $1.5T$). By this method, the first step is to find quantities proportional to Y_m and T, and to deduce these, using appropriate scale factors. For this purpose, a straight line is drawn, tangent to the response curve at the origin of coordinates, and a perpendicular is then erected from an arbitrary point on the axis of abscissae until it intersects the tangent (Fig. VI-1). The side AB of the right-angled triangle OAB is divided, into two, three or four equal parts. A straight line is drawn through the top division point, C, and the origin of coordinates, O, to intersect the transient response curve at point D. The coordinates of the intersection, τ_n and Y_n, are proportional to T and Y_m, respectively. The proportionality (scale) factors, τ_n/T and Y_n/Y_m, may

be found by simultaneously solving Eq. (VI-1) and the equation of the secant:

$$Y = (AC/OA)\tau = (AC/AB)\,(OA/AB)\tau = (AC/AB)\tau Y_m/T$$

To facilitate graphical construction, AC/AB is taken equal to 3/4, 2/3, and 1/2, which respectively yields $Y_n/Y_m = 0.46$, 0.59 and 0.8, and $\tau_n/T = 0.616$, 0.89 and 1.61.

This method may also be used if the tangent is drawn to any point on the response curve, provided that the part of the curve used lies to the right of the point of tangency, that is, in the ordinate range $Y-Y_t$ and in the abscissa range $\tau-\tau_t$, where Y_t and τ_t are the ordinate and abscissa of the point of tangency. Thus, the numerical values of Y_m and T found from the tangent drawn at the origin of coordinates may always be verified, using tangents to the transient response curve at other points.

This method is advantageous in cases where the objective is to plot a family of response curves for a set of values of some variable (which is typical of many chemical-engineering studies). To achieve this objective, it will suffice to plot one response curve spanning the complete time interval (up to $3T$). The static characteristics and time constants of the remaining curves may then be found from their initial portions. With extended transients, this approach will save time which would otherwise be spent on the experimental determination of the response curves.

These response curves are important in the control of chemical-engineering processes such as those taking place in absorption columns, the static and dynamic properties of which range between wide limits, depending on the flow characteristics prevailing in the column.

VI-2. SCALE-UP IN REACTOR DESIGN

The objective of scale-up in reactor design is to determine a criterion or criteria on which to base the transfer of pilot-scale plant data onto a full-scale industrial unit.

Criteria of similarity. Some physical processes taking place in a single phase may be scaled up, using the principles of physical modeling. This technique is based on criteria of geometric and chemical similarity derived from differential equations which describe the process in question, or from dimensional analysis of the process variables.

Unfortunately, as already stated (see p. 14), physical modeling when applied to complex (notably, chemical) processes usually falls short of the objective sought. Yet, consideration of the appropriate differential equations at steady state for the conservation of mass, momentum and thermal energy, with allowance for chemical change, has led to several dimensionless groups. These groups must be equal for both the model and the prototype for complete similarity to exist on scale-up. Six of these dimensionless groups examined below are the Damkohler numbers (Da_I, Da_{II}, Da_{III}, Da_{IV}),[2] the contact (Co) number, and the equilibrium (Pa) number. The manner in which they are derived will be clear from reference to Table VI-1.

Table VI-1

Basic Dimensionless Groups of Chemical Similarity

Equation of conservation of mass

Rate of change with time	Rate of change due to convection	Rate of change due to diffusion	Rate of change due to chemical reaction
$-(dc/d\tau)$	$-(w\ \mathrm{grad})c$	$+D(\mathrm{div\ grad})c$	$+w_r$
c/τ	wc/l	Dc/l^2	w_r
		$\mathrm{Da_I} = w_r l/cw$	
		$\mathrm{Da_{II}} = \frac{w_r l^2}{cD}$	

Equation of conservation of energy

Rate of change with time	Rate of change due to convection	Rate of change due to thermal conductivity	Rate of change due to chemical reaction
$-(dt/d\tau)$	$-(w\ \mathrm{grad})t$	$+a(\mathrm{div\ grad})t$	$+qw_r/c_p\varrho g$
t/τ	wt/l	at/l^2	$q = w_r/c_p\varrho g$
		$\mathrm{Da_{III}} = \frac{qw_r l}{c_p\varrho g w \Delta t}$	
		$\mathrm{Da_{IV}} = \frac{qw_r l^2}{\lambda \Delta t}$	

Equation of reaction kinetics

Resultant rate of reaction	Rate of forward reaction	Rate of reverse reaction
$dc/d\tau$	$+k_f c_{A_1}^{\alpha_1} \cdot c_{A_2}^{\alpha_2} \cdots$	$k_r c_{B_1}^{\beta_1} \cdot c_{B_2}^{\beta_2} \cdots$
c/τ	$k_f c_A^{\Sigma\alpha}$	$k_r c_B^{\Sigma\beta}$
$\mathrm{Co} = k_f c_A^{\Sigma\alpha - 1} \tau$		$\mathrm{Pa} = \frac{k_r c_B^{\Sigma\beta}}{k_f c_A^{\Sigma\alpha}}$

Note. In the above equations, a single arrow points to the denominator, and a double arrow to the numerator.

From the very appearance of the dimensionless groups it is easily seen that they cannot be satisfied at the same time, because the controlling linear dimension l enters them to both the first and the second power. Furthermore, these groups are incompatible with those of physical similitude, such as the Reynolds number, which reveal a different dependence on the linear velocity of the stream.

For example, each of Re and Da_I cannot be equal for both the model and the prototype at the same time, because the linear velocity entering both groups depends differently on the linear dimension also entering both of these numbers. For Re be the same in the model and the prototype, the linear velocity must be inversely proportional to the linear dimension. For Da_I to be the same in the model and the prototype, the linear velocity must vary directly as the linear dimension. Thus, a direct modeling of chemical processes on the basis of common similarity equations is unfeasible; only approximate modeling based on scale-up equations can be realized.

Scale-up in relation to various factors. Quite frequently, two identical reaction systems (say, a pilot-scale plant and a full-scale commercial unit or even two identical commercial reactors) show different performances. This difference in performance stems from differences in the flow patterns in the reactors, in the kinetics of the process, catalyst efficiency, etc. Since pure kinetics can hardly be divorced from physical effects, we may use the method (already described on p. 292) for determining the efficiency of a reactor or a system of reactors (arranged in series, parallel, etc.).

It should also be remembered that in different reactors fluid elements will reside different intervals of time; in other words, statistically residence time will be different and can be estimated only on the basis of the response curve of a system. Therefore, if the model and the prototype are to give the same yield of the wanted product, both should have the same residence time distribution or the same response curve.

The effect of longitudinal mixing may be minimized and the velocity profile may be smoothened through the use of higher flow velocities or packing. Swirl in mixing may be avoided by provision of baffles which additionally secure hydrodynamic reproducibility.

With reactions which give up or absorb much heat, scale-up (even under conditions of geometric similarity) may impair conditions for heat input or removal because the ratio of the heat transfer surface area to the reactor volume is reduced.

In the case of exothermal reactions, identical conditions for heat transfer in both the model and the prototype can be obtained only if both have the same thermal stability coefficient (see below). In fulfilling this requirement, it may be necessary to adjust the heat transfer surface area (by, say, introducing external heat exchangers).

As an alternative, a reactor carrying out a strongly exothermic reaction may be divided into several small-size reactors. In this way, the ratio of the external heat transfer surface area to the reactor volume will be increased and an excessive temperature rise in the reactor avoided. Practically, a reactor may be a system of slim-diameter tubes. The tube diameter is chosen so that the difference in temperature between the stream core inside the tube and the wall will be maintained within the limits corresponding to a maximum yield.

In scaling up a reactor carrying out a strongly exothermic reaction, complications due to a pronounced temperature profile may be avoided by using

as the model an element of the prototype if the latter is made up of several elements (a suitable example is a reactor built up of a system of catalyst-filled tubes; one of these tubes may well serve as the model).

Coefficients of process stability. The scale-up of exothermic processes is greatly facilitated through the use of the coefficient of thermal stability. This coefficient, symbolized as β, is defined[3,4] as the ratio of the slope ($\tan \alpha_2$) of the line representing heat removal (due to the heat-transfer medium and changes in enthalpy) to the slope ($\tan \alpha_1$) of the line representing heat generation (by the reaction) at the intersection of the two lines plotted on the T-versus-Q coordinates:

$$\beta = \tan \alpha_2 / \tan \alpha_1 \qquad \text{(VI-2)}$$

At $\beta > 1$, the process is stable; at $\beta < 1$, it is unstable. The stability condition can be satisfied by linearizing the heat generation (Q_g) and heat removal (Q_r) lines in the vicinity of the equilibrium state, T_S.

Mathematically, the thermal stability coefficient may be justified as follows. Upon linearization, the Q_g-*vs*-T and Q_r-*vs*-T lines may be described by equations of the form

$$Q_g = Q_S + \tan \alpha_1 (T - T_S) \qquad \text{(VI-3)}$$

$$Q_r = Q_S + \tan \alpha_2 (T - T_S) \qquad \text{(VI-4)}$$

where Q_S is the heat flow at the intersection of the Q_g and Q_r lines.

At each instant, the difference between the heat generated and the heat removed is proportional to the rate of change in reactor temperature:

$$Q_g - Q_r = A(dT/d\tau) \qquad \text{(VI-5)}$$

where A is the total heat capacity of the stock in the effective volume of the reactor.

Substituting Eqs. (VI-3) and (VI-4) in Eq. (VI-5) and separating the variables, we get

$$\frac{dT}{T - T_S} = \frac{\tan \alpha_1 - \tan \alpha_2}{A} d\tau$$

or, upon integration

$$T - T_S = C \exp\left(\frac{\tan \alpha_1 - \tan \alpha_2}{A}\right) \qquad \text{(VI-6)}$$

where the constant C is found from the initial conditions in each particular case.

From Eq. (VI-6) it is seen that the difference between the equilibrium and actual temperature decreases if

$$\frac{\tan \alpha_1 - \tan \alpha_2}{A} < 0 \qquad \text{(VI-7)}$$

the rate of decrease being the greater, the greater the absolute value of the left-hand side of Eq. (VI-7).

On setting

$$\beta' = \frac{\tan \alpha_2 - \tan \alpha_1}{A} \qquad \text{(VI-8)}$$

we may say that in Eq. (VI-7) the coefficient β' describes the stability of a process: the greater the value of β', the greater the process stability. At $\beta' = 0$, the process is on the verge of stability; at $\beta' < 0$, the process is unstable, the instability increasing with increasing absolute value of β'.

Noting Eq. (VI-2), Eq. (VI-8) may be re-written as

$$\beta' = \frac{\tan \alpha_1 (\beta - 1)}{A} \tag{VI-9}$$

that is, the coefficient β differs from the coefficient β' by the factor $\tan \alpha_1 / A$. In cases where the coefficient β is used to estimate the stability of the model and prototype, scaling up will increase both $\tan \alpha_1$ and A by the same factor, and their ratio will remain unchanged. This is an indication that the relation between β and β' is univalued, but related to the scale of the process. Therefore, in analysing chemical reactors for stability for the purpose of scale-up, we may well use the coefficient β.

Let β^* designate the stability of the prototype reactor and β the stability of the model. Then, in scaling up, we obtain the *transition stability coefficient* defined as

$$\delta = \beta^* / \beta \tag{VI-10}$$

At $\delta = 1$, both the model and the prototype are similarly stable; at $\delta > 1$, the prototype has a greater stability than the model; at $\delta < 1$, the reverse is true.

In order that the transition stability coefficient may be used for scaling up, the designer must have at his disposal a well-worked out process proceeding in a pilot-scale reactor with a satisfactory performance stability over a temperature interval of interest, at stable component concentrations and other variables that may be used to control the process.

For heterogeneous reactions it is important to know whether the process is controlled by diffusion, kinetics, or both. A method by which the effect of diffusional resistance may be eliminated from laboratory kinetic data for heterogeneous chemical reactions has been described earlier (see p. 385). This method should also be used in scaling up heterogeneous reactors. In some cases a process may be confined to the desired region by controlling hydrodynamic conditions.

The wall effect. As a rule, the model and the prototype use the same catalyst (that is, a catalyst of the same particle size) or the same type of packing. Therefore, the volume elements formed by adjacent catalyst particles or packing units remain the same in the model and the prototype. Yet, the designer should be aware of what is called the wall effect, that is, the change in the ratio of the wall surface area to the reactor volume, which is especially marked in the case of small values of d_a/d_p, where d_a is the diameter of the apparatus and d_p is that of a particle.

The ratio of the wall surface area to the reactor volume is inevitably changed with changes in reactor size. Therefore, the wall effect must be estimated already when deriving kinetic equations, for a set of values of the

ratio. Of course, the wall material must be the same in the model and the prototype reactor.

With the wall effect taken care of, the data obtained on the model can be extended onto the prototype, provided the experiments are conducted under unvarying conditions (that is, at the constant loading per cross-sectional area of the apparatus, constant temperature, constant concentration, etc.) and the ratio d_a/d_p is sufficiently large.

Accumulation of impurities. No accumulation of unwanted products may be noted during a single passage of reactants through a reactor. In commercial processes with recycling, however, the accumulation of unwanted products may well become a problem. This is why work on models should include extended experiments with recycling.

Reactor size and derivation of scale-up equations. As a first approximation, the following scale-up relationships between the model and the prototype may be recommended for use in deciding on the reactor size (at least, in preliminary considerations).[2]

In order to secure the same residence time in the model and in the prototype (that is, the same response), the following equalities must be satisfied:

$$(\mathrm{Da_I})_m = (\mathrm{Da_I})_p \tag{VI-11}$$

$$\frac{w_{rm} l_m}{c_{Am} w_m} = \frac{w_{rp} l_p}{c_{Ap} w_p} \tag{VI-12}$$

where the subscripts "m" and "p" apply to the model and the prototype, respectively.

Cancelling out the physical constants and noting that the concentration (initial or final) is the same for the model and the prototype, we get for $\mathrm{Da_I}$:

$$l_m/w_m = l_p/w_p$$

It follows from the above equation that the residence time in the model and the prototype must be the same.

If a heterogeneous reaction takes place in a purely kinetic region, its scale-up equation will contain the catalyst activity, ν, and the volumetric velocity. Then,

$$(Da_{\mathrm{I}})_m = (Da_{\mathrm{I}})_p$$

or

$$\frac{k_m f(c_A)_m \nu_m}{w_m} = \frac{k_p f(c_A)_p \nu_p}{w_p} \tag{VI-13}$$

where k is the rate constant per unit surface area of catalyst.

Introducing the volumetric velocity V, we get

$$\frac{k_m f(c_A)_m \nu_m}{(d_p)_m V_m} = \frac{k_p f(c_A)_p \nu_p}{(d_p)_p V_p} \tag{VI-14}$$

At $\nu_m/\nu_p = 1$ and $(d_p)_m = (d_p)_p$ (the particle size is assumed to be the same, because any change in this variable will usually entail a change in the activity of the catalyst) we have

$$V_m = V_p \tag{VI-15}$$

that is, the volumetric velocity must be the same for the model and the prototype.

In deriving a scale-up equation for a chemical reaction in a kinetic region, it has also been proposed to allow for heat transfer through the use of Da_{IV} in combination with the Nusselt number, Nu. We shall derive such an equation for a homogeneous reaction in a tubular reactor.

On equating the expressions for the model and the prototype

$$(Da_{IV})_m/\mathrm{Nu}_m = (Da_{IV})_p/\mathrm{Nu}_p$$

we get

$$q_m w_{rm} d_m^2/\lambda_m \Delta t_m \,\mathrm{Nu}_m = q_p w_{rp} d_p^2/\lambda_p \Delta t_p \,\mathrm{Nu}_p \qquad \text{(VI-16)}$$

where d_m and d_p are the diameters of the tubular reactors used as model and prototype, respectively. Assuming that the amount of product discharged from the prototype is n times the amount yielded by the model, we find

$$n d_m^2 w_m = d_p^2 w_p \qquad \text{(VI-17)}$$

whence

$$n = d_p^2 w_p / d_m^2 w_m \qquad \text{(VI-18)}$$

Recalling also that Da_I must be the same for the model and the prototype, we get

$$w_{rm} l_m / c_{Am} w_m = w_{rp} l_p / c_{Ap} w_p \qquad \text{(VI-19)}$$

Besides, the same yield from the model and the prototype can be secured on the condition that the temperature rise will be the same in both. Therefore, for a tubular reactor at

$$\mathrm{Nu} = \text{constant}\ \mathrm{Re}^{0.8} \qquad \text{(VI-20)}$$

from Eq. (VI-16) we get

$$d_m^{1.2}/w_m^{0.8} = d_p^{1.2}/w_p^{0.8} \qquad \text{(VI-21)}$$

It follows from Eq. (VI-19) that

$$l_m/w_m = l_p/w_p \qquad \text{(VI-22)}$$

Solving Eqs. (VI-17), (V-21) and (VI-22) simultaneously, we finally get

$$\begin{aligned} d_p &= d_m n^{0.286} \\ l_p &= l_m n^{0.428} \\ w_p &= w_p n^{0.428} \end{aligned} \qquad \text{(VI-23)}$$

In conclusion, we shall derive scale-up equations for a homogeneous gas-phase reaction in a flow tubular reactor. It should be remembered that the pressure drop must be the same for the model and the prototype. Otherwise, in the reactor with a greater pressure drop the gas stream will be in an accelerated motion, and the residence time will decrease. The difference in pressure drop may be neglected only when the total pressure in a system is great in comparison with the pressure lost.

The coefficient of friction for the gas phase may be defined as

$$\Delta P = c_1 \lambda \frac{l}{d} w^2 \tag{VI-24}$$

on setting

$$\lambda = c_2 Re^{-m} = c_3 (wd)^{-m} \tag{VI-25}$$

and noting that

$$V_q = c_4 d^2 w \tag{VI-26}$$

where c_1 through c_j are constants.

On solving Eqs. (VI-24) through (VI-26), we get

$$l_p/l_m = (d_p/d_m)^{(1+m)/(3-m)} \tag{VI-27}$$

$$(V_q)_p/(V_q)_m = (d_p/d_m)^{(7-m)/(3-m)} \tag{VI-28}$$

For turbulent flow m may be taken to be equal to 0.16. Substituting this value into Eqs. (VI-27) and (VI-28), we find

$$l_p/l_m = (d_p/d_m)^{0.41} \tag{VI-29}$$

$$(V_q)_p/(V_q)_m = (d_p/d_m)^{2.41} \tag{VI-30}$$

Thus, the ratio of the model to prototype dimension at right angles to the direction of flow must exceed that of the dimensions in the direction of flow. In other words, the ratio of length to diameter for the model reactor should be greater than that for the prototype.

Under conditions of laminar flow in both reactors, on the basis of Poiseuille's law we may similarly derive the following scale-up equation:

$$d_p/d_m = \left[\frac{(V_q)_p}{(V_q)_m}\right]^{1/3} \tag{VI-31}$$

Since the reactor length ratio is equal to the reactor diameter ratio, a complete geometric similarity must be retained in this case. Besides, since the ratio of volumetric flow rates is equal to that of the cubes of reactor diameters, the volumetric flow rate must be proportional to the reactor volume.

In the processes of absorption, extraction and rectification with chemical reactions, the latter usually proceed in a region having a finite depth and adjacent to, rather than on, the interface. This is why chemical change and diffusion take place at the same time rather than consecutively. Because of this the diffusional stream of the solute continually decreases on passage through the diffusion region in the liquid phase.

In the case of gas-liquid, vapour-liquid or liquid-liquid reactions, identical flow conditions can be obtained in the model and the prototype only if the variables listed below have the same (idem) values:[6]

$$\frac{w}{w_{inv}} = idem \tag{VI-32}$$

and

$$\frac{1+f_p}{1+f_m} = idem$$

where w and w_{inv} are the given and inverse velocities in a system, f_p and f_m are the hydrodynamic factors of the two-phase system in the prototype and model, respectively, expressing the kinetic energy of the streams in them.[6]

For packed towers, the hydrodynamic factor has the form

$$f = \beta(L/G)^m (\nu_g/\nu_l)^n (\mu_g/\mu_l)^p \left(\frac{\sigma_{1-2}}{\sigma_{1-b}+\sigma_{2-b}}\right)^q \qquad \text{(VI-33)}$$

where L and G are the mass flow rates of the streams, ν_g and ν_l are the specific weights of the continuous and dispersed phases, μ_g and μ_l are the viscosities of the continuous and dispersed phases, σ_{1-2} is the interfacial tension, σ_{1-b} and σ_{2-b} are the surface tensions of the continuous and dispersed phases.

When the same systems are processed in the model and the prototype, the scaling-up of packed towers at the point of inversion reduces to satisfying the following conditions:

– for column diameters:

$$d_{K1}/d_{K2} = (a_1/a_2)^{0.25} (F_{v2}/F_{v1})^{0.75} \qquad \text{(VI-34)}$$

– for pressure drops:

$$\Delta P_1/\Delta P_2 = (a_1/a_2)^{0.3} (F_{v2}/F_{v1})^{0.3} \qquad \text{(VI-35)}$$

where a is the packing surface area per unit volume of reactor, m^2/m^3; F_v is the fraction voids of the packed section, m^3/m^3.

Example VI-1. A laboratory-scale reactor (a tube with a diameter of 25 mm, filled to a height of 38 mm with catalyst particles measuring 6.35 mm across) gives a fractional conversion of 99% at a volumetric velocity of 0.076 m^3/h (the mass flow rate is $G = 239$ kg m^{-2} h^{-1}). Determine the depth of the catalyst bed required to achieve the same fractional conversion in a tubular reactor with a diameter of 35 mm, at a volumetric velocity of 113 m^3/h ($G = 2670$ kg m^{-2} h^{-1}). The reaction is first-order at constant volume under isothermal conditions. The viscosity is $\mu = 0.01$ centipoise.

Solution. To begin with, we find the Reynolds number for the 25-mm reactor:

$$\mathrm{Re} = \frac{Gd_p}{8600\mu g} = \frac{239\times 0.05635\times 9.810}{3600\times 0.01\times 9.81} = 42.2$$

The longitudinal dispersion coefficient for the entire reactor is

$$\frac{D_L d}{W d_p L} = 0.5\times 0.00635 \div 0.038 = 0.0833$$

From Fig. IV-2, the ratio of the volume of the experimental reactor to that of plug-flow reactor is

$$V_R/V_d = 1.35$$

The residence time for the experimental reactor is given by

$$V_R/V_q = 0.212\times10^{-4} \div 0.076 = 2.78\times10^{-4}\,\text{h}$$

The residence time for the respective plug-flow reactor is

$$2.78\times10^{-4} \div 1.35 = 2.045\times10^{-4}\,\text{h}$$

For a full-scale commercial reactor:

$$\text{Re} = Gd_r/3600\mu g = \frac{2670 \cdot 0.0635 \cdot 9810}{3600 \cdot 0.01 \cdot 9.81} = 471$$

while the local longitudinal dispersion coefficient is

$$D_L/wd_p = 0.55$$

Since the height of the catalyst bed is unknown, calculations are carried out by the method of successive approximations.

Assuming that the commercial reactor is a plug-flow unit and using the residence time found earlier for this type of reactor, we find that the height of the catalyst bed should be

$$2.055\times15^{-4}\times0.073 \div 113$$

where 0.073 is the cross-sectional area of the reactor. Hence, $L = 0.315$ m.

The longitudinal dispersion coefficient for the entire reactor length is

$$(D_L/wd_p)\,(d/L) = 0.55\times0.00635 \div 0.315 = 0.0111$$

Referring to Fig. IV-2, it is seen that for this value of D_L/wL the ratio $V_R/V_m = 1.03 \approx 1$.

Tests confirm the assumption of a plug-flow pattern.

The above example shows that backmixing is negligible in the commercial reactor. It has been shown earlier convincingly that laboratory data on longitudinal mixing cannot be extended to commercial units unless their response curves are plotted, because the laboratory and commercial apparatus may greatly differ in flow patterns.

Application of batch-reactor data to a cascade. Sometimes the need arises to apply kinetic data derived on a batch reactor to a continuous process, usually a cascade of stirred-tank reactors.

This transition is sufficiently realiable if each unit in the cascade approaches a complete-mixing model which finds a practical embodiment in baffled stirred tanks operating under conditions of strong turbulence ($\text{Re} = nd^2/\nu < 10$), where n is the rpm of the agitator, d is the agitator diameter, that is the diameter of the area swept by the agitator blades in metres, and ν is the kinetic viscosity of the fluid in m^2/s).

The transition is based on the use of concentration-*vs*-time plots and residence time distributions for a cascade of well-stirred reactors. The sequence of steps involved is illustrated by the example that follows.

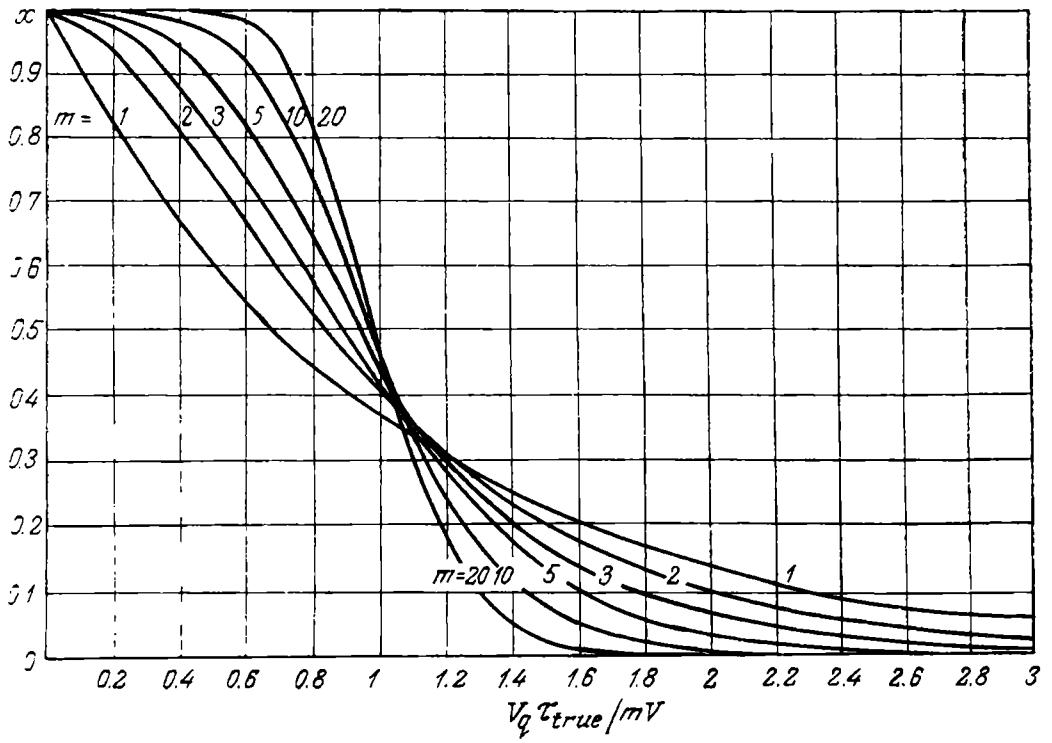

Fig. VI-2. Time distribution of products in a consecutive reaction of the type $A \rightarrow B \rightarrow R \rightarrow S$

Example VI-2.[7] A batch reactor carries out a consecutive reaction of the type $A \rightarrow B \rightarrow R \rightarrow S$. Using the experimental data, develop a continuous process in a cascade of m reactors.

Solution. (1) The experimental data are plotted as concentration-versus-time ($c - \tau$) curves (Fig. VI-2).

(2) Changes in concentrations are measured at sufficiently small time intervals which fit straight segments on the concentration distribution curves. In our example, the time interval is 0.2 h.

(3) From the fractional conversion-versus-dimensionless time plot based on Eq. (IV-55), we find the true residence time for a cascade of reactors (Fig. VI-3).

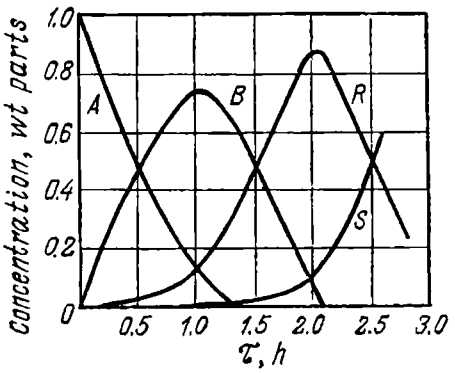

Fig. VI-3. Fractional conversion as a function of dimensionless resistance time

In using these plots, we first set the ratio of the total reactor volume in litres, V (the cascade is assumed to consist of equal-size tanks) to the hourly volumetric throughput, V_h, to be equal to $V/V_h = 0.75\tau$ (where τ is the nominal process time found from the c-vs-τ plot for a given product at a relatively low fractional conver-

sion, x) with consideration of an economic separation of reaction products. Model studies have shown that high product yields are economically optimal usually at a low fractional conversion.

(4) Now a table (Table VI-2) is compiled in order to find the true residence time, $\Delta\tau_{true}$, averaged over the time interval selected.

Table VI-2

τ	c_A	$\bar{c}_A$	c_B	$\bar{c}_B$	c_R	$\bar{c}_R$	c_S	$\bar{c}_S$	V_h/V	τ_{true}	$\Delta\tau_{true}$
0	1.0		0		0		0		0	1.00	0.05
		0.90		0.10		0		0			
0.2	0.8		0.2		0		0		0.266	0.95	
		0.70		0.290		0.01		0			0.17
0.4	0.6		0.380		0.02		0		0.532	0.78	
		0.508		0.450		0.028		0			0.21
0.6	0.415		0.528		0.035		0		0.798	0.57	
		0.337		0.598		0.049		0			0.19
0.8	0.26		0.668		0.062		0		1.06	0.38	
		0.196		0.703		0.106		1.001			0.14
1.0	0.132		0.739		0.150		0.002		1.330	0.24	
		0.086		0.729		0.194		0.005			0.10
1.2	0.04		0.72		0.238		0.008		1.60	0.14	
		0.02		0.655		0.312		0.009			0.06
1.4	0		0.590		0.385		0.010		1.86	0.08	
				0.498		0.473		0.015			0.03
1.6	—	—	0.406		0.560		0.020		2.13	0.05	
				0.322		0.640		0.036			0.02
1.8	—		0.238		0.72		0.053		2.40	0.03	
				0.149		0.80		0.83			0.015
2.0	—		0.060		0.88		0.112		2.66	0.015	
		—		0.03		0.82		0.169			0.009
2.2	—		0		0.76		0.226		2.92	0.006	
		—	—	—		0.67		0.313			0.003
2.4	—			—	0.58		0.405		3.19	0.003	
		—		—		0.49		0.502			0.001
2.6	—			—	0.40		0.600		3.46	0.002	
2.8	—		—			0.30		0.700			0.001
					0.20		0.800		3.72	0.001	
3.0	—		—			0.10		0.900			0.0002
					0		1		3.99	0.0008	
3.2									4.25		
3.4									4.52		$\sum =$
											0.9992

The reactant and product concentrations are entered in Table VI-2 as weight fractions. The values of τ_{true} are found from the plot for $m = 3$, $m = 4$, and $m = 5$ (three variants are computed), and finally $\Delta\tau_{true}$ is found over the selected time interval.

Table VI-2 has been compiled correctly, if the sum of the average concentrations of all components in each row and the sums of all values of $\Delta\tau_{true}$ approach unity. If the total reactor volume has been chosen too small, the ratio V_h/V will be excessive, and $\sum \Delta\tau_{true}$ will approach unity before all concentrations have been depleted. This is an indication that the residence time is so short that the side products have no time to form in appreciable amounts.

(5) In order to find the average composition for each reaction component leaving the flow reactor, a table of $(\Delta\tau_{true}c)$ should be compiled (Table VI-3). The table has been compiled correctly, if $\sum \Delta\tau_{true}c$, for each component approaches unity.

VI-3. USE OF EXPERIMENTAL DATA FOR REACTOR OPERATION ANALYSIS AND OPTIMAL DESIGN

It has been stated more than once that the flow pattern in a reactor can be established, that is, a reactor can be identified as belonging to a particular model by the response curve method, applied under actual conditions. Response curves may also be utilized to determine the effectiveness of a reactor and how closely the operating conditions of a commercial unit approach those of the applicable model.

As a rule, optimum operating conditions for a commercial reactor are worked out in a number of steps as follows.

(1) Experiments are carried out on a pilot-scale unit.

(2) The basic process variables are expressed mathematically in terms of cost and experimental data.

(3) The operating conditions of the commercial unit are optimized.

Although any of these steps may be carried out separately, they are ordinarily used in the above combination.

We shall trace the calculation of a chemical reactor, taking a contact-catalytic process as an example. This class of processes has been chosen for its complexity.

The conditions essential to the optimization of catalytic reactors have been analysed by several investigators.[8] Theoretically optimum conditions (that is, those under which the desired product yields and process selectivity are attained at a minimum catalyst cost) may be derived from kinetic data. For example, for one reversible reaction the optimum temperature is brought down with a rise in fractional conversion (Fig. VI-4*a*). A similar situation may arise in the case of two consecutive reactions (Fig. VI-4*b*), although for two simultaneous reactions the optimum temperature may rise (Fig. VI-4*c*). Further examples of optimum temperature conditions are shown in Fig. VI-4.

Table VI-3

$\tau_2-\tau_1$	$\Delta\tau_{true}$	$\bar{c}_A$	$\Delta\tau_{true}\bar{c}_A$	$\bar{c}_B$	$\Delta\tau_{true}\bar{c}_B$	$\bar{c}_R$	$\Delta\tau_{true}\bar{c}_R$	$\bar{c}_S$	$\Delta\tau_{true}\bar{c}_S$
0.2–0	0.05	0.90	0.0450	0.10	0.0050	0	0	0	0
0.4–0.2	0.17	0.70	0.1190	0.290	0.0492	0.01	0.0017	0	0
0.6–0.4	0.21	0.508	0.1068	0.450	0.0945	0.028	0.0059	0	0
0.8–0.6	0.19	0.337	0.0640	0.598	0.1137	0.049	0.0093	0	0
1.0–0.8	0.14	0.196	0.0274	0.703	0.0984	0.106	0.0148	0.001	0.0001
1.2–1.0	0.10	0.086	0.0086	0.729	0.0729	0.194	0.0194	0.005	0.0005
1.4–1.2	0.06	0.020	0.0012	0.655	0.0393	0.312	0.0187	0.009	0.0005
1.6–1.4	0.03	0.0	0	0.498	0.0149	0.473	0.0142	0.015	0.0005
1.8–1.6	0.02	—	—	0.322	0.0064	0.640	0.0128	0.036	0.0007
2.0–1.8	0.015	—	—	0.149	0.0022	0.800	0.0120	0.083	0.0012
2.2–2.0	0.009	—	—	0.030	0.0003	0.820	0.0074	0.169	0.0015
2.4–2.2	0.003	—	—	0	—	0.670	0.0020	0.316	0.0009
2.6–2.4	0.001	—	—	—	—	0.490	0.0005	0.502	0.0005
2.8–2.6	0.001	—	—	—	—	0.300	0.0003	0.700	0.0007
3.0–2.8	0.0002	—	—	—	—	0.100	—	0.900	0.0002
3.2–3.0	—	—	—	—	—	0	—	—	—
	0.9992	—	0.3720	—	0.4968	—	0.1190	—	0.0073

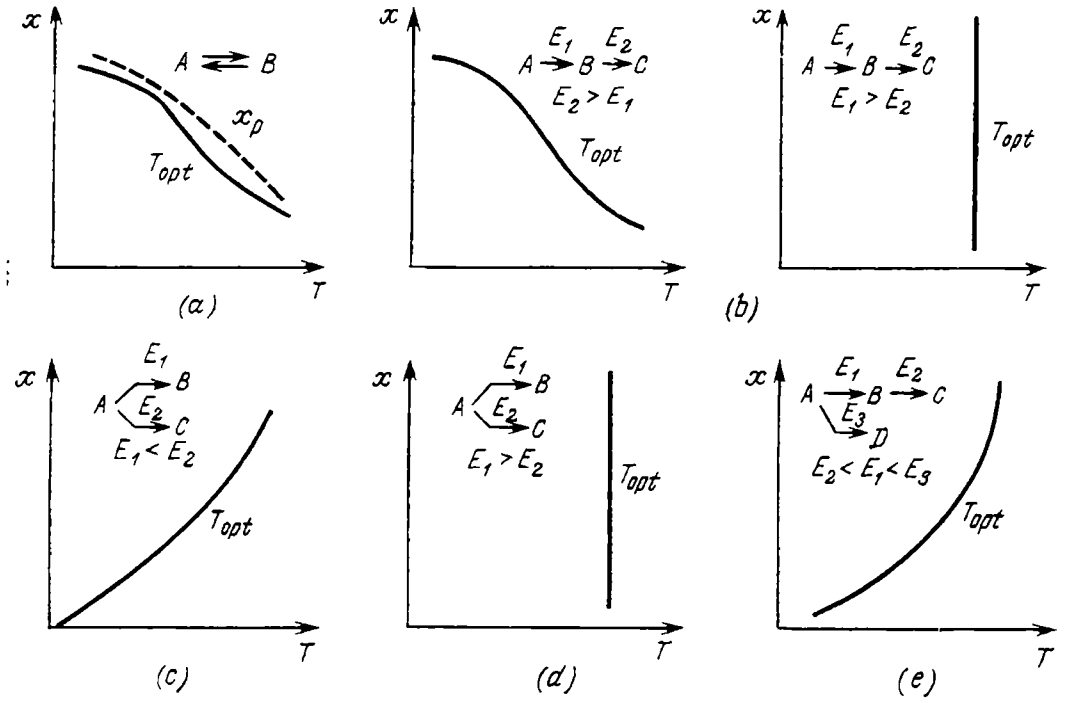

Fig. VI.4. Optimum temperature
B — wanted product

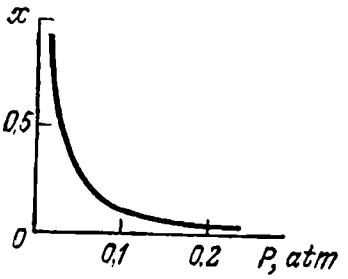

Fig. VI-5. Optimum pressure for the hydrogenation of butylene

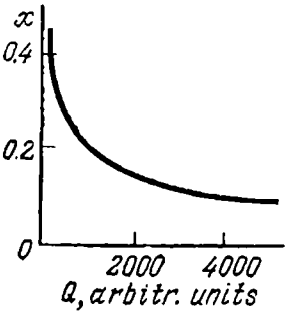

Fig. VI-6. Rate of heat generation under optimum conditions of ammonia synthesis

In addition to an optimum temperature, optimum pressures (Fig. VI-5) and optimum feed compositions are determined for a variety of conditions. This can conveniently be done through the use of plots relating temperature T, pressure P, composition or heat generation Q to fractional conversion, x.

A plot of changes in the rate of heat generation as a function of fractional conversion at an optimum temperature in the synthesis of ammonia is shown in Fig. VI-6. Using this plot, it is an easy matter to determine how heat removal should be varied across the catalyst bed in order that the process can proceed at the highest rate. Conversely, plotting the progress of a process on these charts, one may see how closely it is to its theoretical

performance. Generally, theoretical performance is one of the principal criteria in the choice of a reactor type. It is a sort of reference for the changes that should be made in the conduct of the process with an increase in the degree of conversion.

Another consideration in the choice of a reactor type is whether the process in question proceeds in a diffusion or a kinetic region. Processes with external diffusion can be conducted in reactors with one, fairly low adiabatic bed of catalyst. The effect of pore diffusional resistance on the process at the catalyst surface must also be tested. If one simple reaction or several simultaneous reactions are involved, pore diffusional resistance will only reduce the observed activity of the catalyst. If, however, the wanted product undergoes a partial change in the reactor (as may be the case with consecutive reactions yielding an intermediate product), pore diffusional resistance may appreciably impair the selectivity of the process. To avoid this, the catalyst pellets may have to be reduced in size, and this may affect the choice of a reactor type.

Once the physical and chemical relationships have been established, the process in the catalyst bed is described mathematically. A contact apparatus may consist of several contact stages each with a catalyst bed of its own, heat exchangers, agitators and other accessories. Therefore, different mathematical descriptions apply to the process and the apparatus.

A catalyst bed may be visualized as a quasi-homogeneous system; the course of the contact-catalytic process in this system is controlled by process variables.

Process variables. These include constraints on: (a) the temperature range set by the thermal strength of the catalyst, its chemical properties, activity, etc.; (b) the gas composition which should be such that no explosion hazard may arise or any damage to the catalyst done; (c) pressure; and (d) the maximum hydraulic resistance.

An important factor is the choice between a flow or a recycle process scheme. A recycle scheme is applied to processes in which a single passage of a gas through the reactor results in an insignificant fractional conversion, that is to processes (1) with a sudden decrease in reaction rate with degree of conversion; (2) with reversible exothermic reactions, if sufficiently high levels of conversion are attained only at low temperatures and (3) with an intermediate product decomposing when the process is carried to completion. It should be remembered, however, that if the reacting gas contains inert impurities, these will tend to accumulate in the recycle. To sum up, a recycle process scheme may be used for processes with a low fractional conversion of gases free from inert impurities.

With exothermic reactions, a major difficulty may arise because of the need to remove the heat of reaction. This difficulty may be circumvented by the use of a fluidized catalyst bed in which the particles are maintained at a high rate of circulation which renders the rate of heat generation uniform throughout the bed, thereby facilitating heat removal. Also, the coefficient of heat transfer to the cooling surface is higher from a fluidized

than from a fixed bed. Thus, fluidized-bed systems are especially adapted to processes with high rates of heat generation. Among these systems, the best performance (a small cooling surface area coupled with a high rate of reaction) is shown by units operating under regulated unsteady-state conditions.

The advantages of fluidized-bed systems, however, become less pronounced with an increase in pressure. Firstly, the coefficient of heat transfer from a fluidized bed becomes comparable with that from a fixed bed; secondly, the fluidized bed expands excessively and, as a consequence, rate of reaction per unit of reactor volume decreases.

Fluidization is also advantageous in systems where the catalyst is continually circulated between a regeneration and a reacting unit (as in the dehydrogenation of butane). It should be remembered, however, that catalysts are subject to attrition because of which the apparatus is eroded, the product picks up catalyst dust, and fine filters have to be added to the system.

To sum up, fluidization should preferably be applied to catalytic processes where it is essential to control temperature within a narrow range, to remove a large quantity of heat per unit volume, and to circulate the catalyst. It may also be applied to processes taking place under conditions of pore diffusion; in such cases, however, the need arises for a catalyst capable of withstanding attrition.

Example VI-3. Find the quantity of catalyst needed for an isothermal reactor.

The calculation usually involves the following steps:[9]

(1) A rate equation is learned or derived, using laboratory kinetic experiments (described earlier). For example, an empirical rate equation of the form

$$w_r = \frac{k_1 P_A P_B}{1 + k_2 P_A + k_3 P_R}$$

for contact-catalytic processes proceeding in a gas phase (reactions of the type $A+B \rightleftarrows R+S$) may be developed by such methods.

(2) The reaction rate constants k_1, k_2 and k_3 are computed or determined at the reaction temperature.

(3) On the basis of a material balance, the partial pressures P_A and P_B of components A and B are found for a set of values of fractional conversion, x, from zero to the desired one.

(4) The reaction rate, w_r, is found for each value of x.

(5) The reciprocal reaction rate, $1/w_r$, is plotted against the fractional conversion, x.

(6) The area under the $1/w_r$-*vs*-x curve is found over the interval from $x = 0$ to its final value.

(7) The area thus found gives G/V_m. Since the molar volume, V_m, of the gas passing through the reactor is known, the amount G of catalyst can readily be found.

(8) From G thus found, the catalyst volume is determined, and the cross-

sectional area of the apparatus is calculated on the basis of the desired throughput. Once the volume and cross-sectional area of the reacting unit are found, the height of the catalyst bed and that of the apparatus are computed.

We shall apply the above sequence to a flow reactor with a fixed catalyst bed under isothermal conditions ($t = 540°C$) for a reaction of the type $A+B \rightleftarrows R+S$, proceeding in the gas phase at 2 atm. The molecular weights of the components are as follows: $M_A = 80$, $M_B = 20$, $M_R = 40$, and $M_S = 60$. The product R should be formed at a rate of 450 kg/h. The fractional conversion should be 95%. The hydraulic resistance of the bed may be neglected.

Solution. (1) Kinetic experiments have revealed that the reaction rate may be expressed by the empirical equation given above.

(2) The rate constants at 540°C (with partial pressure expressed in atmospheres) are as follows: $k_1 = 0.595$, $k_2 = 4.46$ and $k_3 = 41.65$.

(3) Since the fractional conversion, x, is defined as the ratio of kg moles of product to kg moles of feed, then the number of kg moles for A and B is $(1-x)$, and for the product R it is x.

Hence, the partial pressures may be expressed as follows:

Component	kg moles	Mole fraction	Partial pressure
A	$1-x$	$(1-x)/2$	$1-x$
B	$1-x$	$(1-x)/2$	$1-x$
R	x	$x/2$	x
S	x	$x/2$	x

(4) The reaction rates for various values of x are summarized in Table VI-4, and the values of w_r and $1/w_r$ in Table VI-5.

Table VI-4

$x(P_R)$	P_A^{1-x}, P_B	$P_A P_B$	$k_1 P_A P_B$	$k_2 P_A$
0.1	0.9	0.81	0.482	4.01
0.2	0.8	0.64	0.381	3.57
0.3	0.7	0.49	0.291	3.12
0.4	0.6	0.36	0.244	2.68
0.5	0.5	0.25	0.149	2.23
0.6	0.4	0.16	0.0952	1.785
0.7	0.3	0.09	0.0535	1.340
0.8	0.2	0.04	0.0238	0.3890
0.9	0.1	0.01	0.00595	0.446
0.92	0.08	0.0064	0.00381	0.357
0.94	0.06	0.0036	0.00214	0.268
0.95	0.05	0.0025	0.00149	0.223

Table VI-5

k_3P_R	$1+k_2P_A+k_3P_R$	w_r	$1/w_r$
4.165	9.175	0.0524	19.05
8.340	12.91	0.0295	33.85
12.50	16.62	0.0175	57.10
16.65	20.33	0.0106	94.90
20.80	24.03	0.0062	161.5
24.98	27.77	0.0034	291.5
29.15	31.49	0.0017	588.0
33.25	35.14	6.8×10^{-4}	1.475
37.42	38.87	1.5×10^{-4}	6.530
38.25	39.61	9.6×10^{-5}	10.400
39.15	40.42	5.3×10^{-5}	18.900
39.60	40.88	3.6×10^{-5}	27.400

It follows from Table VI-5 that at $x = 0.8$ and higher, the rate of reaction drastically slows down. Therefore, in order to determine G/V_m, we plot two graphs, one for x in the range from 0 to 0.8 and the other, in the range

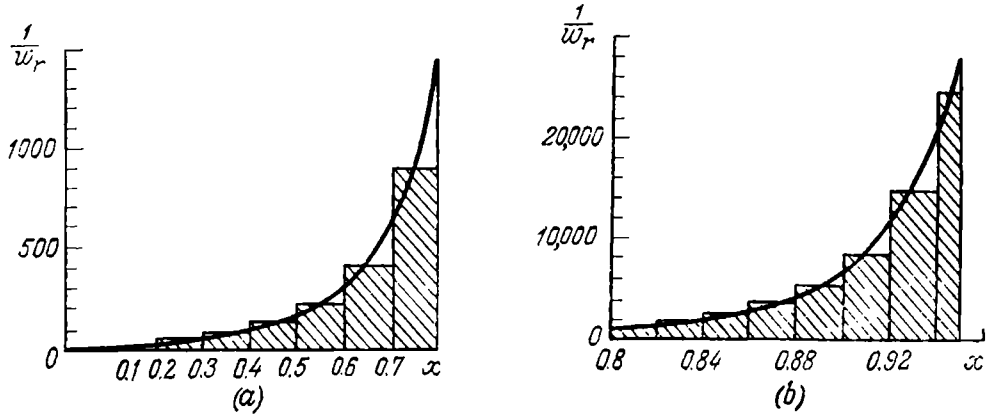

Fig. VI-7. Plot of $1/w_r$ as a function of fractional conversion
(*a*) $x = 0.1$-0.8; (*b*) $x = 0.8$-0.95

from 0.8 to 0.95 (Fig. VI-7). From the plot of Fig. VI-7*a* we find the area under the curve to be equal to 179. According to the plot of Fig. VI-7*b*, the area under the curve is 915. The total area is 1094.

On the basis of the above plots, we have

$$G/V_m = \int_0^{0.95} \partial x/w_r \approx 1094$$

From the statement of the problem, $R = 450$ kg/h and $M_R = 40$. Hence, the amount of R is 11.25 kg mole h^{-1}.

The amount of A needed is

$$11.25 \div 0.95 = 12.9 \text{ kg mole } h^{-1}$$

The amount of catalyst needed is

$$G = 1094 \times 12.9 = 14{,}200 \text{ kg}$$

The bulk density of catalyst is $\varrho_B = 1250$ kg/m^3; hence, the catalyst volume is

$$V_{cat} = 14{,}200 \div 1250 = 11.4 \text{ m}^3$$

Now, a physical embodiment for the reacting unit can be considered. Assuming that the unit is operating under conditions of complete mixing, then

$$G/V_m = x_f/w_{r,f}$$

where x_f and $w_{r,f}$ are the final values of fractional conversion and final reaction rate ($x_f = 95\%$).

At $x = 0.95$, from Tables VI-4 and VI-5 we find

$$P_A = 0.05; \quad P_R = 0.95; \quad k_1 P_A P_B = 0.00149; \quad k_2 P_A = 0.223;$$

$$k_3 P_R = 39.60; \quad w_{r,f} = 3.6 \times 10^{-5}; \quad \text{and}$$

$$G/V_m = x_f/w_{r,f} = 0.95 \times 3.6 \times 10^{-5} = 26{,}000 \text{ kg of catalyst per kg mole } A \text{ h}^{-1}$$

Thus, the needed amount of catalyst is

$$26{,}000 \times 12.9 = 336{,}000 \text{ kg}$$

This is about 25 times as great as is needed for a flow reactor without backmixing. The effect of backmixing can be minimized by the use of a high catalyst bed and sectionalized tubes.

Staging of the catalyst bed. In cases where the bulk of catalyst is divided into stages by shelves, longitudinal mixing in the reaction mixture can only take place within each stage; the gradient in gas concentration between stages can be equalized by the gas bubbles breaking through and by the bulk stream. Such a staged reactor comes very closely to a cascade of well-stirred reactors. A major problem with this scheme is that of distributing the total amount of catalyst among stages.[12]

As an example, we shall consider a first-order reaction. Under conditions of complete mixing, the amount of product formed on each stage is equal to the reactant concentration at the exit from a given stage multiplied by the catalyst volume in that stage and by the rate constant per unit of catalyst volume.

The following notation will be used: V_q, the volumetric velocity of the gas mixture, m^3 s^{-1}; c_0, the initial concentration of the reactant, kg mole m^{-3};

x_i, the fractional conversion in an ith stage; n, the total number of stages; k, the rate constant, s^{-1}; V_i, the catalyst volume in an ith stage, m^3; and V, the total catalyst volume, m^3.

The amount of material formed on each stage is given by

$$\left.\begin{aligned} V_q c_0 x_1 &= k c_0 (1-x_1) V_1 \\ V_q c_0 (x_2 - x_1) &= k c_0 (1-x_2) V_2 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ V_q c_0 (x_n - x_{n-1}) &= k c_0 (1-x_n) V_n \end{aligned}\right\} \qquad \text{(VI-36)}$$

On transforming and adding together, we get

$$\frac{x_n - x_{n-1}}{1-x_n} + \ldots + \frac{x_2 - x_1}{1-x_2} + \frac{x_1}{1-x_1} = \frac{k}{V_q} V \qquad \text{(VI-37)}$$

In determining the fractional conversion for each stage under conditions of a minimum total catalyst volume, we get

$$x_i = 1-(1-x_n)^{i/n} \qquad \text{(VI-38)}$$

Under the circumstances, each stage holds the same amount of catalyst, or

$$V_1 = V_2 = \ldots = V_n \qquad \text{(VI-39)}$$

$$V = nV_1 \qquad \text{(VI-40)}$$

For a first-order reaction retarded by the presence of a product, the optimum distribution of fractional conversion among stages is the same, but the amount of catalyst on each stage increases in proportion to the fractional conversion

$$V_1 : V_2 : V_3 : \ldots : V_n = x_1 : x_2 : x_3 : \ldots : x_n \qquad \text{(VI-41)}$$

$$V = V_1 \frac{n - \dfrac{1-x_1}{x_1} x_n}{x_1} \qquad \text{(VI-42)}$$

For non-isothermal processes, a more elaborate expression is derived. Instead of Eq. (VI-38), we then get:[12]

$$x_i = 1 - \frac{k_1^{i-1}}{k_2 k_3 \ldots k_i} (1 - x_n^{i/n}) \qquad \text{(VI-43)}$$

where $k_1, k_2, \ldots, k_i$ are the rate constants.

In such a case, each stage holds a different amount of catalyst. The greater the number of stages, the closer to unity the ratio of the needed catalyst amounts per stage (Table VI-6).

The amount of catalyst needed for an adiabatic reactor is found as follows:

(1) The applicable rate equation must be known in advance.

(2) The rate constants k_1, k_2 and k_3 are computed or determined within the temperature limits where the process is planned to proceed.

Table VI-6

Ratio of Catalyst Amounts per Stage

Final conversion	Number of stages					
	1	2	3	5	10	∞
	First-order reaction					
0.9	3.9	1.85	1.5	1.27	1.15	1
0.98	12.5	3.15	2.1	1.53	1.21	1
	First-order reaction retarded by product					
0.9	5.9	2.4	1.8	1.45	1.26	1
0.98	16.4	3.9	2.4	1.7	1.33	1

(3) The heat of reaction is determined over the entire temperature range of the process.

(4) The heat capicity (at constant volume) is found over the entire temperrature range of the process.

(5) The heats of reaction and heat capacities thus found are tabulated in order to plot the fractional conversion, x, against temperature, t, and the partial pressures P_A, P_B, etc. are then found for a set of values of x from zero to the desired value (see Example VI-3).

(6) The rate of reaction, w_r, is computed and tabulated for each value of x. Use is made of the rate constant, k, at the temperature corresponding to each value of x on the curve.

(7) The reciprocal rate of reaction, $1/w_r$, is plotted as a function of the fractional conversion. The area under the $1/w_r$-*vs*-x curve in the interval from $x = 0$ to its desired value gives the value of the integral

$$G/V_m = \int_0^x dx/w_r$$

(8) From the integral thus evaluated and the value of V_m, the needed amount, G, of catalyst is determined.

(9) From the amount of catalyst thus found, the catalyst volume is computed and the cross-sectional area of the apparatus is determined on the basis of the specified throughput. Then the depth of the catalyst bed and the height of the reactor are found.

(10) If the reaction is exothermic, the reactor is tested for thermal stability.

Example VI-4. Optimum operating conditions will be found for a catalytic contactor used to oxidize nitrogen oxide at a rate of 50 tons per day. The nitrogen oxide for the contactor is produced in a very diluted state, by the oxidation of atmospheric nitrogen in a regenerated moving bed by the Vis-

consin process. The procedure will be presented on the basis of the process analysis and optimization carried out by Hougen.[10]

Solution. In order to optimize the process, we must examine 17 variables, namely: (1) feed composition; (2) type of catalyst; (3) feed temperature; (4) dew point of the feed; (5) reactor temperature; (6) fraction of the recycled gas; (7) reactor exit pressure; (8) reduction in catalyst activity; (9) mass flow rate of the bulk gas; (10) catalyst particle (pellet) size; (11) height of the catalyst bed; (12) diameter of the catalyst bed; (13) number of catalyst contact stages; (14) fractional conversion of NO; (15) maximum charge of catalyst; (16) pressure differential (gradient) across the catalyst bed; (17) overall height of the reactor.

Of the 17 variables listed above, eight can be found from preliminary experiments and from past plant records, without recourse to mathematics. Of the remaining nine, four variables are independent and five are dependent. The independent variables are: catalyst particle (pellet) size, mass flow rate of the bulk gas, fractional conversion, and number of catalyst-bed stages. The dependent variables are: diameter and depth of the catalyst bed, reactor height, maximum charge of catalyst, and pressure gradient across the catalyst bed.

Choice of the first eight variables. (1) The composition of the entering gas, which is the first of the variables under consideration, can be found from the equilibrium composition (achieved in the Visconsin process) in the regenerated moving bed of a pelletized catalyst.

In the regenerated catalyst bed, nitrogen is oxidized to nitrogen oxide at 2200°C; at this temperature the reaction proceeds at a very high rate, and thermodynamic equilibrium is reached at a nitrogen oxide content of about 15%.

Since the reaction is endothermic, the fractional conversion can be raised only with a rise in temperature; however, 2200°C is the limit for heat-resistant catalyst pellets. A regenerative heating system ensures that a high temperature can be obtained even by burning a gas of low calorific value. The entering hot gas is passed in turn through two regeneratively-heated pelletized beds, because of which the temperature in the combustion zone rises to 2200°C at an equilibrium NO content of 1.5%. Attempts to enrich the gas by liquefaction and subsequent distillation have proved expensive, and these methods are not examined.

(2) The next point is the choice of a catalyst. Experimentation has shown silica gel and activated carbon to be the best. In the case at hand activated carbon is chosen because its mass needed to reach the desired fractional conversion is 0.1%, and it is less sensitive to the presence of water vapour. The danger that the adsorbed NO_2 might ignite it can be avoided by forcing a continuous current of air through the catalyst bed at plant shut-down. No tendency to ignition has been reported in any of the experiments at plant shut-down, even without a current of air. Some grades of silica gel have also proved no less efficient per unit mass than activated carbon.

(3) An increase in temperature has but an insignificant effect on the rate

of the catalytic oxidation of nitrogen oxide. Whatever increase there could be in the rate of the reaction on the surface of the catalyst with increasing temperature it would be counteracted by a similar effect of temperature on the adsorption of nitrogen oxide. However, it is important to cool the gas in order that water vapour can be removed by condensation. Thus, the temperature of the entering gas depends on that of cooling water: at a water temperature of 20°C and a temperature gradient of 10°C between the gas and water at the exit of a countercurrent heat-exchanger, the temperature of the gas leaving the condenser is 30°C. Any further cooling by refrigeration would be economically unattractive.

(4) The fourth variable is the dew point of the entering gas. Water vapour should preferably be removed at a temperature below that at which natural condensation occurs. At a dew point of 0°C, the rate of reaction is half as great as it is when use is made of dry air. The reduction in moisture content to a dew point of 30°C is an arbitrary decision. This dew point can be obtained with activated alumina as adsorbent. It would be preferable to find an optimum dew point from data gathered in an activated-alumina adsorber if there were any.

(5) The fifth problem is to determine the range of temperature control in the reactor, with a heat-exchanger built into its base. For complete conversion of the entering gas, the temperature rise is about 28°C. Since the rate of reaction depends but little on temperature, provision of a heat exchanger at the reactor base would give no advantage. Thus, internal temperature control is unecessary, and the reaction proceeds adiabatically.

(6) The sixth variable is the desired degree of recycling. Since the final fractional conversion is 98%, recycling appears to be undesirable.

(7) The seventh point is the pressure at the exit from the reactor. Doubling exit pressure would nearly halve the catalyst mass needed. However, a prohibitive amount of mechanical energy would be required to compress a diluted gas carrying as little as 1.5% NO in order to supply 50 tons of nitrogen oxide per day. In the light of past experience, operation at atmospheric pressure is preferable.

It may be remarked that compression would be economically advantageous, if the energy spent could be recovered during expansion. However, the energy involved in alternating compression and expansion is too small for this scheme to be workable. Thus, the pressure of the gas leaving the reactor must be just sufficient for the gas to pass at a desired velocity through the adsorption and regeneration system which follows the reactor. Precisely this factor is, in the final analysis, a major limitation of the Visconsin process in comparison with the synthesis of ammonia at high pressure.

(8) Since the catalyst is known to retain its activity for years, no extra supply need be envisaged in order to make good any loss in catalyst activity.

Thus, through a detailed consideration and the use of a limited number of experimental data, we have estimated eight important variables, avoiding any mathematical formalism.

Further data. The data needed to optimize the process also include the gas

pressure difference (gradient) across the catalyst bed, heat and mass transfer from the bulk of the gas to the external surface of catalyst particles, heat and mass transfer in the pores of catalyst pellets, model of the surface reaction, and cost data.

The cost items are capital cost, taxes, depreciation, insurance and maintenance cost. These five items are assumed to account for 40% of capital outlays per year. It is also necessary to take into account the cost of the reactor, blower, turbine, catalyst, steam, fuel, power and expenses due to the loss of unconverted nitrogen oxide.

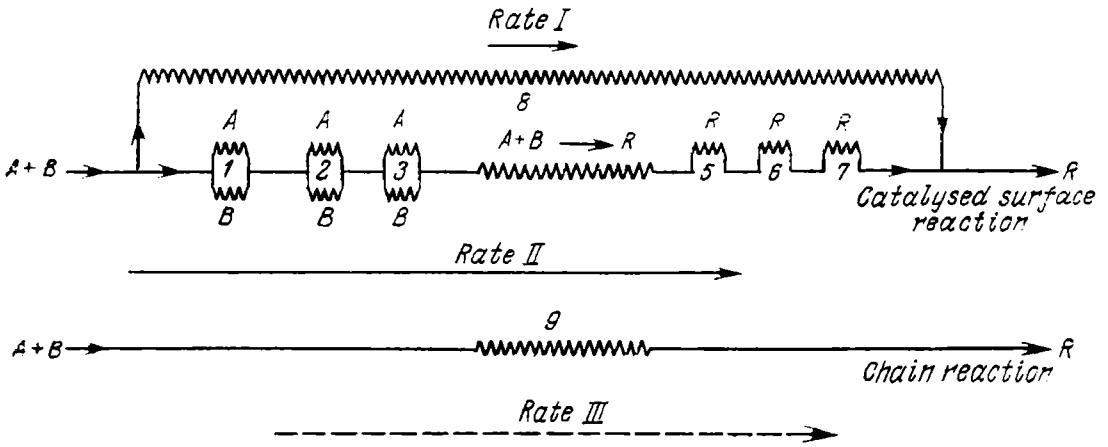

Fig. VI-8. Resistances in a catalytic gas-phase reaction of the type $A+B \rightarrow R$

I – homogeneous reaction (rate may be neglected; a good catalyst is used); *II* – gas-phase reaction over a solid catalyst; *III* – homogeneous chain reaction with free radicals forming on catalyst surface; *1* – diffusional resistance of film to *A* and *B* (a minimum at high mass flow rates); *2* – diffusional resistance in pores to *A* and *B* (a minimum with small pores in pellets); *3* – resistance to adsorption of *A* and *B* (low for good catalysts); *4* – surface resistance to reaction $A+B \rightarrow R$; *5* – resistance to desorption of *R* (considerable in the case of catalyst poisoning); *6* – diffusional resistance in pores to *R* (a minimum with small pores in pellets); *7* – diffusional resistance of film to *R* (a minimum at high rates); *8* – homogeneous reaction (simultaneous with a surface reaction); *9* – homogeneous chain reaction (chain-forming free radicals appear on catalyst surface)

Resistance and process rate. In graphic form, the various resistances that exist during gas-phase reactions in solid-catalyst reactors for a general reaction of the type $A+B \rightarrow R$ are shown in Fig. VI-8. The zig-zag lines give the magnitude of resistances, and the arrows represent process rates. In the figure the rate of a homogeneous reaction is shown negligible. In some reactions, the catalyst serves to form free radicals owing to which a homogeneous reaction will proceed at a very high rate, as shown by the lower line in Fig. VI-8. This rate is left out of consideration in our discussion of oxidation of nitrogen oxide.

Pressure difference (drop) across the catalyst bed. The factor is especially important because of the low NO and NO_2 concentrations and the extremely high concentrations of nitrogen and oxygen that are blown through the catalyst bed. Under the circumstances, a good deal of energy has to be expended even at a conservative pressure drop.

The pressure difference (drop), ΔP, is defined as

$$\Delta P = \frac{\lambda G_g^2 a_V L}{\varepsilon^3 \rho_g g} \quad [\text{kg (f)/m}^2] \qquad (a)$$

where G_g is the mass flow rate of the gas, kg m^{-2} s^{-2}; a_V is the external area per unit volume of the catalyst bed, m^2m^{-3}; L is the height of the catalyst bed, m; ε is the bed porosity, m^3m^{-3}, ρ_g is the gas density, kg m^{-3}; and g is the acceleration due to gravity, m s^{-2}.

The coefficient of friction is defined as

$$\lambda = a(\text{Re})_p^b \qquad (b)$$

where

$(Re)_p$	a	b
3	5.0	−1.0
3-30	3.0	−0.6
30-1000	0.88	−0.23

The Reynolds number is given by

$$(\text{Re})_p = G_g d_p / g\mu_g \qquad (c)$$

where d_p is the diameter of a catalyst particle, m; μ_g is the viscosity of the gas, kg s m^{-2}.

Difference in temperature and pressure between the bulk of the gas and the catalyst surface. The difference in temperature between the bulk of the gas and the catalyst surface is significant only at low velocities of the bulk stream. In the general case, however, this difference must be recognized, since otherwise appreciable errors might creep in when kinetic data are interpreted and, as a consequence, an inapplicable reactor model might be assumed and the rate-controlling step chosen incorrectly.

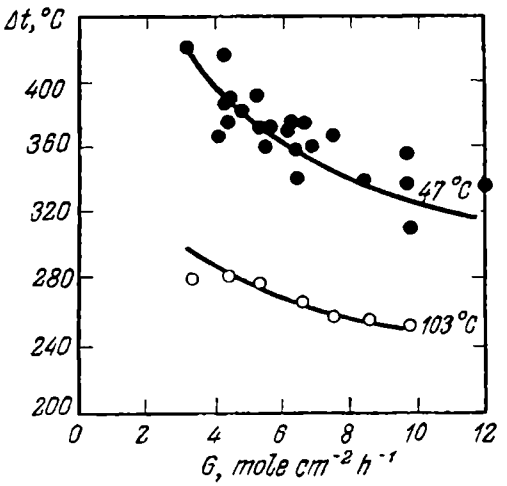

Fig. VI-9. Difference in temperature between catalyst surface and bulk stream (hydrogenation of propylene at 1 atm)

As an example of this type of error source, Fig. VI-9 shows the difference in temperature between the bulk stream and the catalyst surface during the hydrogenation of propylene. Referring to the chart, it is seen that under certain conditions the difference in temperature between the catalyst surface and the bulk of the gas may be as great as 400°C.

The errors stemming from failure to recognize this difference in temperature are shown in Fig. VI-10 for experimental reactions carried out at three different temperature levels of the bulk of the gas. Since a surface reaction proceeds at a faster rate than a reaction in the bulk stream, it would be

more correct to determine the rate of reaction at the surface temperature. Referring to Fig. VI-10, it is seen that the surface temperature is a few hundred degrees higher than that of the bulk stream because the reaction is highly exothermic.

The experimental data obtained at the three levels spread over a wide temperature range, and only a small proportion of reactions occur at the

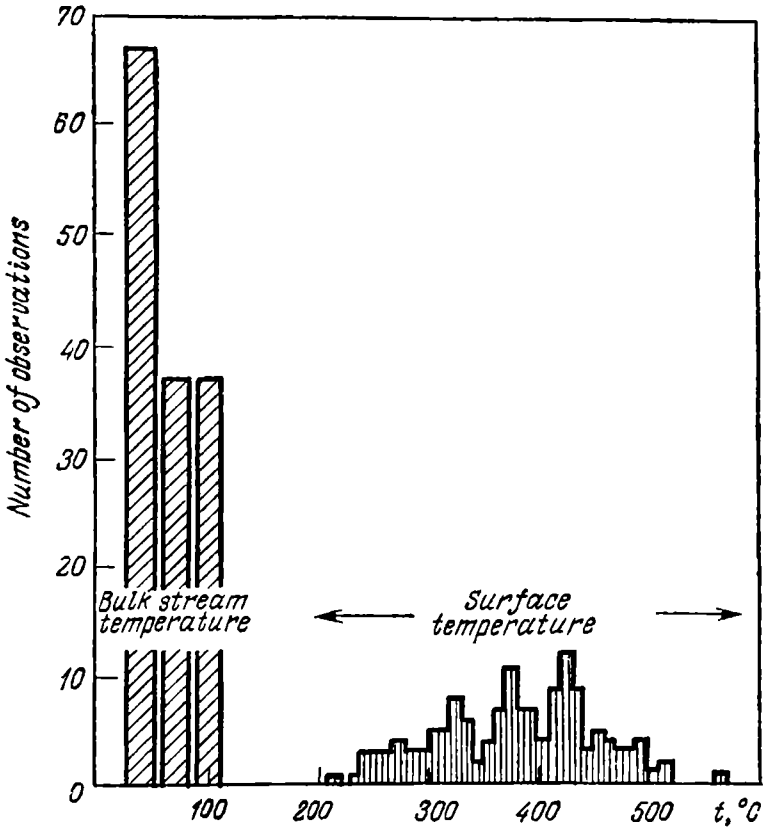

Fig. VI-10. Number of experiments at given temperature levels (catalytic hydrogenation of propylene)

surface temperature level for which the isothermal constants needed for the rate equation are determined.

Calculations of the difference in partial pressure and temperature between the bulk stream and the catalyst surface are extremely complicated. However, they may be simplified through the use of plots in Figs. VI-11 and VI-12. The difference in partial pressure is defined as

$$\Delta P_A = w_r \nu_c / a_V \Phi K_g \qquad (d)$$

where w_r is the rate of the catalytic reaction, kg mole NO converted, h^{-1}, per kg^{-1} of catalyst; ν_c is the bulk density of catalyst, kg m^{-3}, and Φ is the shape factor.

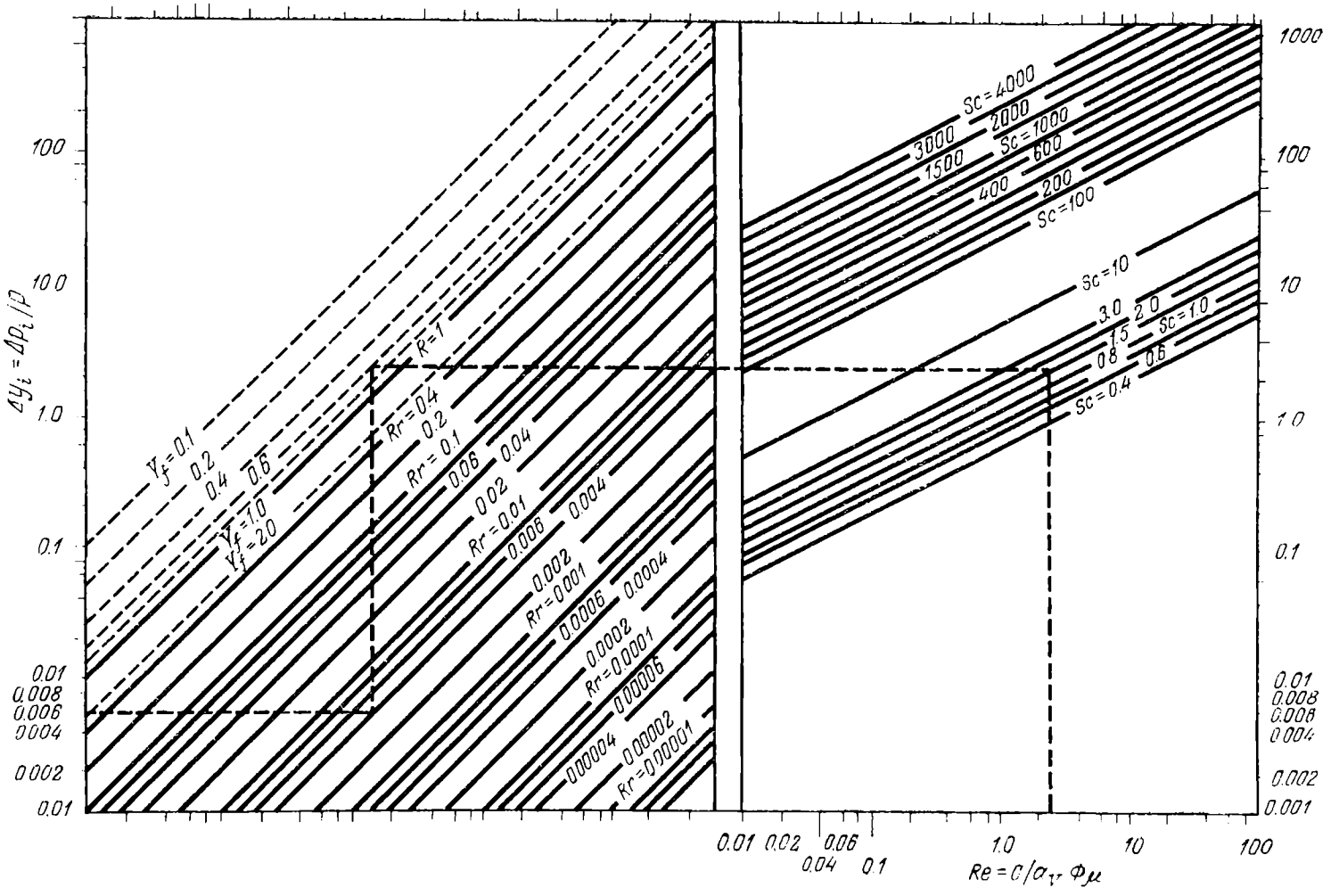

Fig. VI-11. Difference in partial pressure between bulk stream and catalyst pellet surface

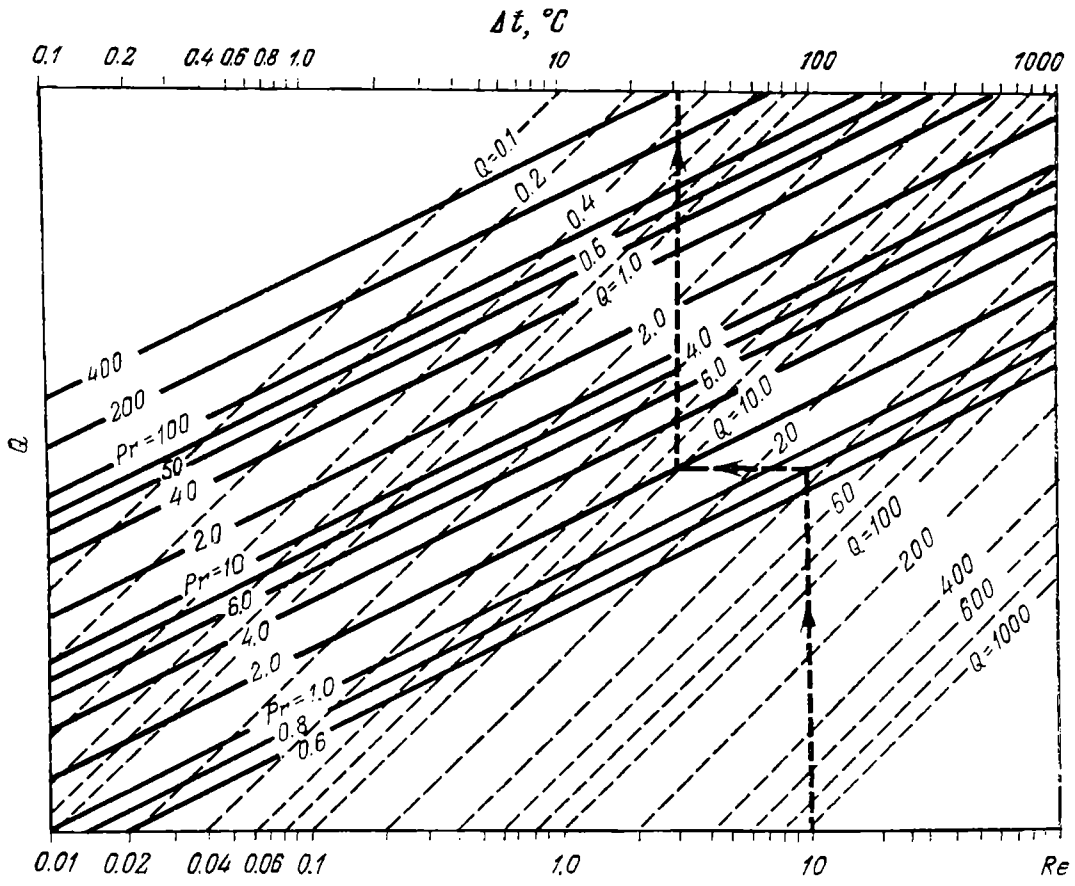

Fig. VI-12. Difference in temperature between bulk stream and catalyst pellet surface

The mass-transfer coefficient, K_g (kg mole m^{-2} h^{-1}) is related the modified mass-transfer coefficient, j_d as

$$j_d = \frac{K_g P_f Sc^{2/3} M_m}{G_m} \qquad (e)$$

where P_f is the partial pressure film factor; $Sc = \mu_g g/\rho_g D_m$ is the Schmidt number; D_m is the molecular diffusivity; M_m is the mean molecular weight of the gas; G_m is the mass flow rate of the gas stream, kg mole m^{-2} h^{-1}.

The factor j_d is related to the Reynolds number, $Re = G_g/a_V \Phi \mu_g g$ as follows

– for $Re < 50$

$$j_d = 0.84(Re)^{-0.51} \qquad (f)$$

– for $Re > 50$

$$j_d = 0.57(Re)^{-0.41} \qquad (g)$$

The rate equation of mass transfer for component A is

$$q_{mA} = K_{rA} a_m \Phi (P_A - P_{Ai}) \qquad (h)$$

The respective equation describing the difference in partial pressure across the gas film is written as

$$\Delta P_A = \left(\frac{q_{mA}\nu_c}{a_m G_m}\right)(j_d)^{-1} P_{fA}\left(\frac{\mu_g g}{\rho_g D_{mA}}\right)^{2/3} \qquad (i)$$

The fraction void per unit mass and unit volume is

$$a_m \nu_c = \frac{6(1-\varepsilon)}{S d_p} = a_V \qquad (j)$$

where S is the spherical shape factor of catalyst particles.

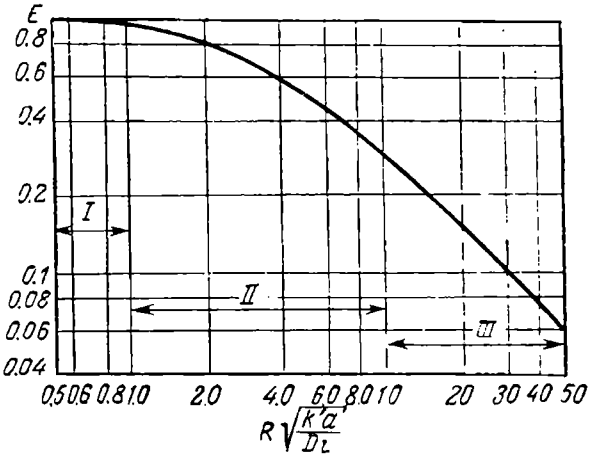

Fig. VI-13. Effectiveness factor as a function of catalyst pellet modulus

I — insignificant diffusional resistance; *II* — intermediate conditions; *III* — internal diffusion as the controlling step; R — pellet radius; k' — reaction rate constant; D_L — pellet diffusivity; a — surface area per unit volume of catalyst pellets

Referring to Fig. VI-13, the most important variables in determining the difference in temperature are the Reynolds number and the quantity of heat, Q, defined as

$$Q = \frac{q_{mA}\Delta H_A}{a_m \Phi c_p G_m} \qquad (k)$$

where ΔH_A is the heat of reaction with respect to component A and c_p is the heat capacity at constant pressure.

It should be noted that for gases the Prandtl number, Pr, has a relatively small effect on the difference temperature.

The difference in partial pressure may be defined in terms of the Reynolds number, Re, and the reaction rate factor defined as

$$R_r = w_r / a_m \Phi G_m \qquad (l)$$

In establishing the reactor model experimentally, it is desirable to keep the difference in temperature and in partial pressure as low as practicable, thereby allowing some uncertainty as regards the conditions on the external catalyst surface. This condition is satisfied at a high mass flow rate of the

gas. The manner in which the difference in partial pressure is estimated is clear from reference to Fig. VI-11.

It involves the following steps: a perpendicular is erected from the Reynolds number, *Re*, laid off as abscissa, until it intersects the line labelled with the respective Schmidt number, whence a line parallel to the axis of abscissae is drawn until it intersects the respective Y_f-line, from which a perpendicular is dropped to locate the applicable R_r-line, whence a line parallel to the axis of abscissae intercepts ΔP_i on the axis of ordinates. The respective difference in partial pressure is found from the plot of Fig. VI-15, in the following steps: starting at a given Reynolds number, one moves until a line labelled with the Prandtl number is intersected, whence the next move is to the respective *Q*-line, and from the *Q*-line towards the upper axis of abscissae, on which the resultant intercept gives the sought difference in temperature, Δt_i.

Effectiveness factor. The effectiveness factor *E*, of the catalyst is defined as the ratio of the actual reaction rate per unit mass of catalyst to the rate which would result if no diffusional resistance were present. Very often, the effectiveness factor, *E*, is found from Thiele's diagram shown in Fig. VI-13. Within interval *I*, pore diffusion resistance is negligible, and the effectiveness factor is close to unity. Within interval *III*, the overall reaction rate is controlled by pore diffusion. In experiments to establish the reactor model, it is desirable to operate within interval *I*.

Thiele's diagram is qualitatively useful in the analysis of conditions under which catalyst pellets differing in size and porosity may be used. However, the diagram is based on the assumption that the catalyst surface adsorbs the reacting gas insignificantly, which is not true. The effectiveness factor for the catalytic oxidation of nitrogen oxide, as adjusted for the effect of surface absorption, is shown in the plot of Fig. VI-14. As is seen, the effec-

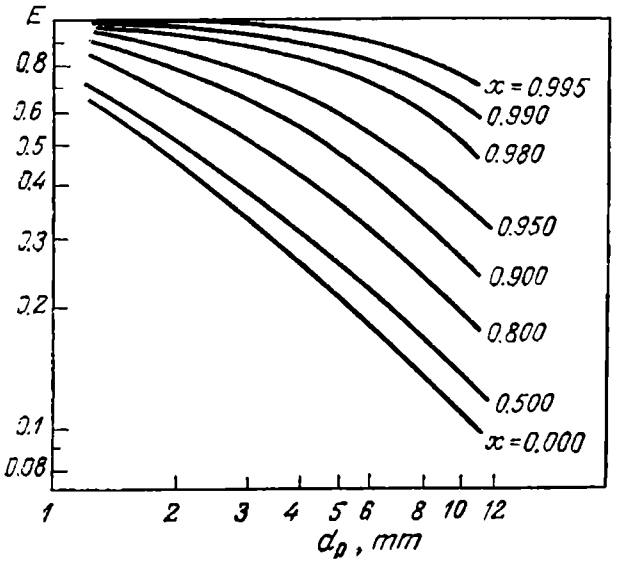

Fig. VI-14. Effectiveness factor as a function of catalyst pellet diameter and fractional conversion in the oxidation of NO

tiveness factor is close to unity for small pellets and gradually decreases with increasing diameter of catalyst pellets. The plot also shows the effect of fractional conversion on the effectiveness factor, which is a minimum at the inlet and tends to unity at the exit.

Establishing the reaction model. In establishing the reaction model by experiment, the following precautions must be made:

(1) the activity of the catalyst must be maintained practically constant;

(2) use should be made of catalyst pellets with a high effectiveness factor, that is, with a high porosity and a small size. This will help to limit the uncertainty in data processing, when high temperature and concentration gradients exist between catalyst pellets;

(3) the resistance to the heat and mass transfer from the bulk of the gas to the catalyst solid surface should be kept to a minimum. This condition is satisfied at high mass flow rates of the diffusing gas;

(4) a plug-flow model under conditions of a steady-state flow should be obtained. Any deviation from plug flow will introduce an amount of uncertainty as regards the flow pattern within the bed;

(5) the difference in pressure between the bulk of the gas and at the catalyst surface should be kept to a low value.

Effect of longitudinal mixing. Under conditions of plug flow, the rate of the catalytic oxidation of nitrogen oxide may be expressed by the following equation where the partial pressures are taken at the external catalyst surface:

$$w_r = G'_m\, dx/dV_R = \frac{P^2_{NO} P_{O_2}}{a + bP_{NO} + cP_{NO_2} + gP_{H_2O}} \qquad (m)$$

where G'_m is the mass flow rate of the feed, kg mole h^{-1}; x is the fractional conversion; and V_R is the reactor volume.

Under conditions of a steady-state plug flow, the reaction rate may be found as the slope of the fractional conversion curve in Fig. VI-15.

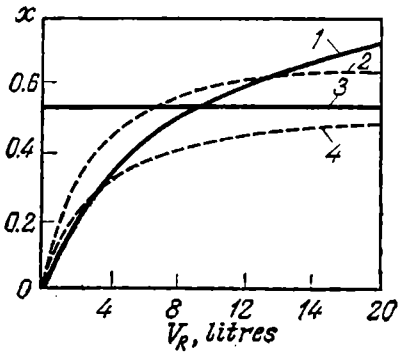

Fig. VI-15. Fractional conversion as a function of reactor volume for a flow reactor, different flow patterns and bed height

1 – plug flow; *2* – incomplete mixing ($L = 0.18$); *3* – complete mixing ($L = 1/l = 0.354$); *4* – channel model ($L = 0.483$)

Under conditions of complete mixing it is obvious that the reaction rate cannot be expressed in terms of the slope of the fractional conversion curve, but it can be found from the equation

$$w_r = G'_m(\Delta x/\Delta V_R)$$

For conditions which lie in between plug flow and complete mixing, the flow pattern becomes indeterminate, and the reaction rate is unknown at any point. Under the circumstances, the reaction rate can in a first approximation be found by interpolation between the extreme values, that is, between that applicable to plug flow, V_{Rb}, and that applicable

to complete mixing, V_{Rm}, and the reactor volume V_R can be deduced from a linear relation of the form

$$V_R = V_{Rb} + eL(V_{Rm} - V_{Rb}) \qquad (n)$$

More accurate results may be obtained by assuming a hybrid model (see p. 117), and its adequacy may be tested by applying a step and an impulse disturbance.

Cost data. The estimated cost of the plant (including capital outlays, taxes, depreciation, insurance and maintenance) may be as high as 40% of the overall investment per year. The cost of a reactor, c_r, depends on its size and the diameter and thickness of its top and bottom; the cost of a blower, c_b, depends on the pressure drop across the reactor and exit pressure; the cost of gas compression, c_g, depends on the amount of power needed to compress the gas adiabatically (that is, the power expended by the associated compressor) and, again, the pressure drop across the reactor. The cost of steam, c_s, is expressed in terms of energy consumed and depends on the pressure drop across the catalyst bed and the pressure of the gas leaving the reactor; the cost of the nitrogen oxide remaining unreacted is c_N, and that of the catalyst is c_c. Then the overall cost of the plant is

$$y = c_r + c_b + c_g + c_s + c_N + c_c$$

The objective of optimization is to minimize this function relative to all independent variables.

Computer calculations. The complex form of the objective function necessitates the use of a digital computer. As a starting step, computation is done for ideal conditions, ignoring the overall pressure drop across the catalyst bed, the differences in pressure and temperature between the bulk of the gas and the external surface of the catalyst and also on the assumption that the effectiveness factor is unity.

Then, all of these factors are included, and y is minimized by the method of steepest descent. The results are given in Figs. VI-16 through VI-22.

Figure VI-16 shows contours of constant cost overlaid on a mass flow rate-versus-particle diameter plot at a fixed fractional conversion. The minimum cost equal to 16,527 roubles is obtained at $G = 1240$ kg m^{-2} h^{-1} and at $d_p = 9$ mm. Fig. VI-17 relates cost and fractional conversion to the size of catalyst particles. Similar results are obtained from Figs VI-20 and VI-21 where the overall cost is plotted against d_p for a set of values of G. It should be noted that some minimum values are obtained at $G = 1240$ kg m^{-2} h^{-1}. The high cost at low mass flow rates is due to an increase in the resistance to heat and mass transfer.

Figures VI-16 through VI-22 also give other combinations of variables used to carry out minimization with respect to fractional conversion, catalyst particle size and mass flow rate. With the cost of catalyst raised 10 times, optimum conditions are secured with small particles and a low catalyst bed. A plot of overall cost as a function of catalyst-bed staging shows that the

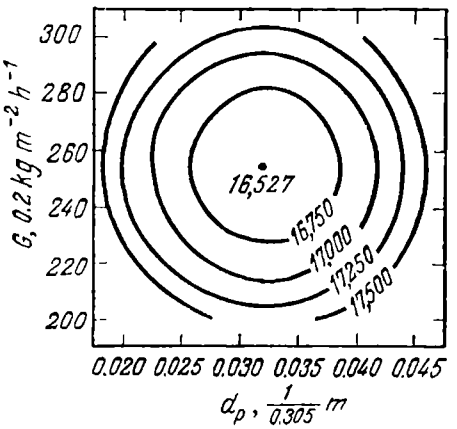

Fig. VI-16. Mass flow rate of gas and cost contours near the optimum (x = constant = 0.9855, number of bed stages, n = 8)

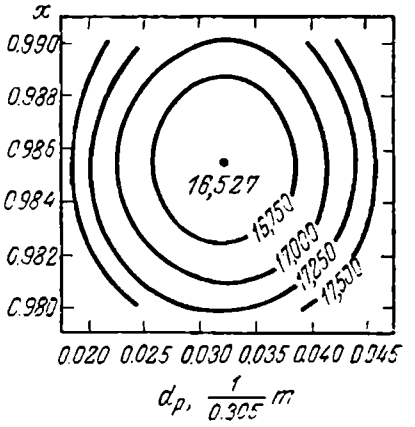

Fig. VI-17. Fractional conversion and cost contours near the optimum (G = 1240 kg m^{-2} h^{-1}, n = 8)

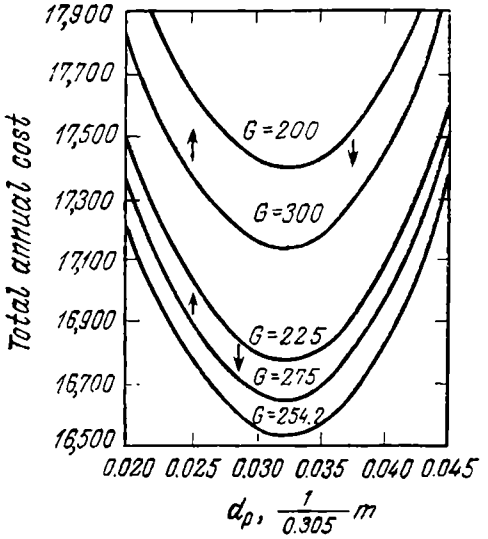

Fig. VI-18. Total annual cost of plant near the optimum (G = = constant; x = 0.9855, n = 8)

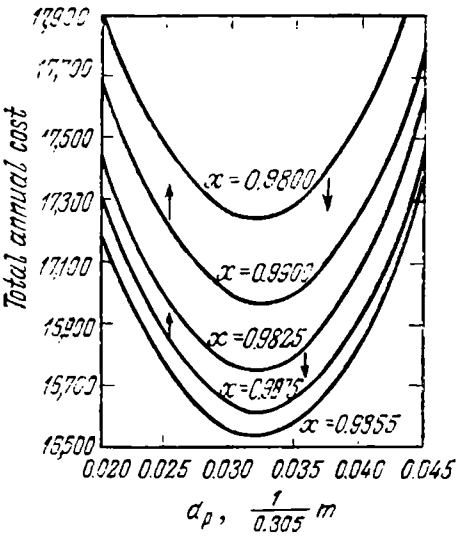

Fig. VI-19. Total annual cost (x = = constant, G = 1240 kg m^{-2} h^{-1}, n = 8)

reactor cost is a minimum with a catalyst bed having eight stages (Fig. VI-22).

Results of optimization. Finally, the optimum conditions may be formulated as follows: (1) inlet feed composition, 1.5%; (2) activated carbon as catalyst; (3) inlet gas temperature, 30°C; (4) the dew point of entering gas, 30°C; (5) operation under adiabatic conditions, because otherwise internal heat exchangers would have to be installed; (6) no gas recycling; (7) exit gas pressure, 0.1 atm (gauge); (8) an insignificant decrease in catalyst activity; (9) the mass flow rate of entering gas, 1240 kg m^{-2} h^{-1}; (10) particle diameter, 9 cm; (11) bed height, 78 cm; (12) reactor diameter, 3.9 mm; (13)

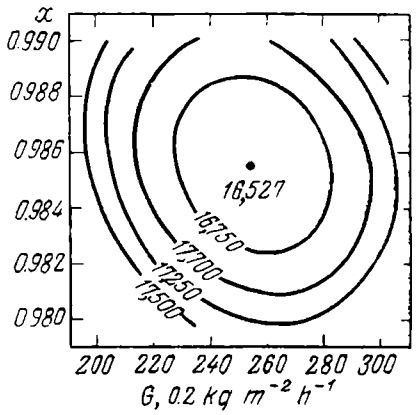

Fig. VI-20. Functional conversion as a function of mass flow rate of gas and cost contours near the optimum (d_p = constant = 9 mm, n = 8)

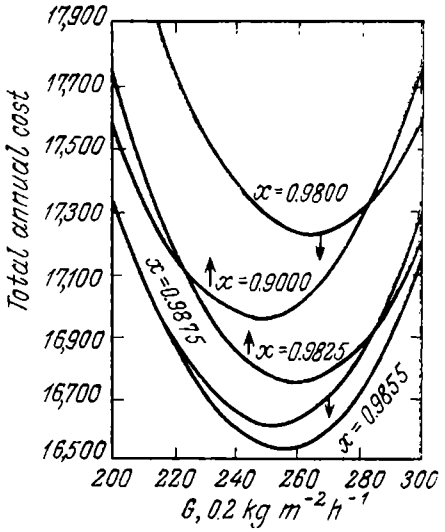

Fig. VI-21. Total annual cost of plant as a function of mass flow rate and fractional conversion (d_p = 9 mm, n = 8)

catalyst-bed stages, 8; (14) overall fractional conversion, 98.6%; (15) catalyst charge, 37.8 kg; (16) pressure drop, 45. mm w.c.; (17) total reactor height, 15 m.

With eight catalyst-bed shelves fitted into a reactor 3.9 m in diameter and 15 m in overall height, a reasonably good design can be obtained. It should be stressed that the reactor will operate economically at a very modest pressure drop (as little as 4.5 mm w.c.) across the catalyst bed, because the NO concentration of the bulk gas is low.

Choice of an optimum operating cycle for a batch reactor carrying out slow processes. We seek an operating cycle that will give a maximum product output per unit time. For the purpose of our discussion, we shall break up a complete cycle into two steps, the change-round (which includes the servicing of the reactor for operation, loading of the feed, raising the feed to conditions needed for the reaction to proceed, and discharge of the product from the reactor) and the reaction proper.

The time taken by each step depends on the character of the chemical process involved. In some cases, the reaction proper may extend over a time interval so long that one has to fix the instant at which to stop the operation, lest the apparatus should move out of an optimum operating range. For example,

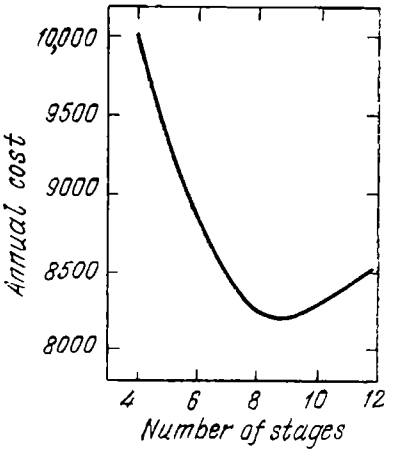

Fig. VI-22. Annual cost of reactor as a function of catalyst stages (x = 0.9855, G = 1240 kg m^{-2} h^{-1}, d_p = 9 mm)

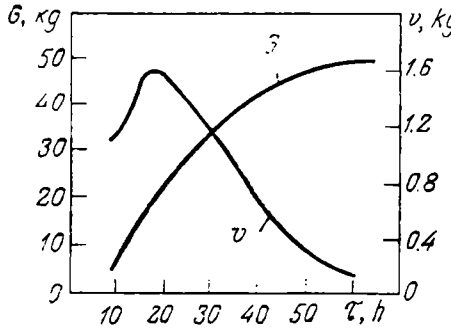

Fig. VI-23. Yield and rate of product formation as functions of reaction time

In fermentation processes the reaction time is considerable in relation to the first step, and the instant at which the operation should be terminated is not clear.

Such a reaction[11] is illustrated in the plot of Fig. VI-23 where the reaction time τ is laid off as abscissa, the product yield G as ordinate on the left, and first derivative, that is the rate of product formation r, as ordinate on the right. Nothing can be gleaned from these curves about the instant at which the throughput will be a maximum or the cost will be a minimum. What is clear is that the rate of product formation is a maximum near the start of the reaction.

At some stage in the process, as is seen, the rate of product formation drops to a point at which the yield of product per unit of reactor volume per unit time is a maximum; at this point the operation may be discontinued for change-round. This is an optimum point in terms of maximum yield. Any further increase could only be obtained at a higher plant cost. This optimum can be found in any one of several methods.

Method 1. The yield of the product is plotted against time (Fig. VI-24). The change-round time is then plotted on the negative direction of the x-axis to locate point A. From this point a straight line is drawn so that it is tangent to the yield curve at point B. The intercept on the x-axis from point B gives the duration of the reaction proper (as is seen, it is 41 hours), while the intercept from point B on the y-axis gives the product yield (43.5 kg).

This method is simple and fast. However, for some curves the point of tangency is difficult to locate.

Method 2. Let G be the amount of product obtained in time τ. If the change-round time is τ_1, the total time needed to obtain the above amount of product will be $(\tau+\tau_1)$. Hence, the amount of product per unit time will be $G_\tau = G/(\tau+\tau_1)$. Taking data from the G-versus-τ curve, we plot G_τ against the reaction time (Fig. VI-25). The peak on the resultant curve gives the maximum time needed to reach a maximum output per unit time (41 hours).

Method 3. If the yield curve can be described by an equation, usually quadratic or cubic (most often for the upper portion of the curve), a solution can be obtained analytically. In the case of a quadratic equation, we get

$$G = B_0 + B_1\tau + B_2\tau^2$$

Solving the above equation simultaneously with the equation

$$G_\tau = G/(\tau+\tau_1)$$

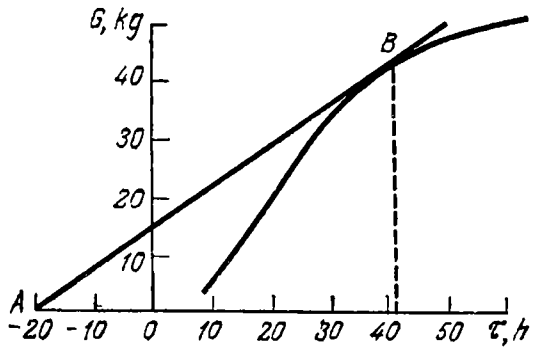

Fig. VI-24. Product yield as a function of time

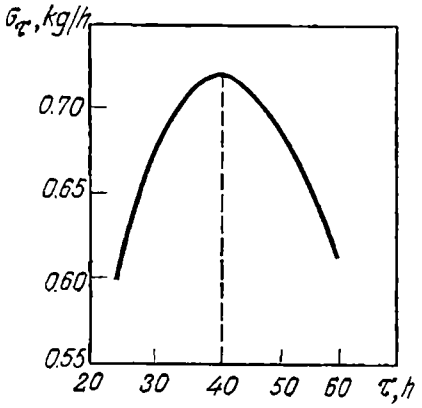

Fig. VI-25. Yield in time units as a function of reaction time

and equating $dG_\tau/d\tau$ to zero, we find the time needed to reach maximum throughput:

$$\tau = -\tau_1 \pm \sqrt{\frac{B_0 - B_1\tau_1 + B_2\tau_1^2}{B_2}}$$

For example, the upper portion of the curve in Fig. VI-24 fits the following equation:

$$G = -17.9 + 2.295\tau - 0.0195\tau^2$$

and the time to maximum throughput is

$$\tau = 40.6 \text{ hours}$$

VI-4. CONTROL OF REACTORS

The variables that may be manipulated to control a given type of reactor usually are: (a) flow rate of reactants; (b) ratio of reactant flow rates; (c) temperature of the heat-transfer medium; (d) flow rate of the heat-transfer fluid.

Control by manipulation of reactant flow rate at the reactor inlet. In this case (Fig. VI-26), use is made of open-loop control (see p. 42). A major advantage of this form of control is simplicity. However, it may only be applied to cases where the fractional conversion is relatively low. At high fractional conversions a relatively small change in x will require a substantial change in the flow rate of reactants, because the fractional conversion decays exponentially.

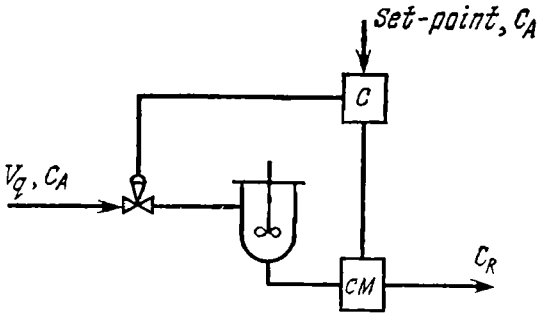

Fig. VI-26. Feed rate control
C – controller, *CM* – concentration meter

Control by manipulation of the ratio of reactant flow rates. This is

a more frequently used scheme of reactor control. It is effected indirectly, as explained below.

As is seen from Fig. VI-27, this is likewise open-loop control. Changes in the flow rate of the controlled stream, A, are measured to control the flow rate of the manipulated stream B. Fig. VI-28 shows a closed-loop control scheme in which the flow rates of both streams are measured, and the controller operates the control valve in accordance with the ratio measured. Although this scheme uses feedback, it provides for an indirect control of the ratio $V_{q,B}/V_{q,A}$, because $V_{q,B}$ is not measured after it is added to $V_{q,A}$.

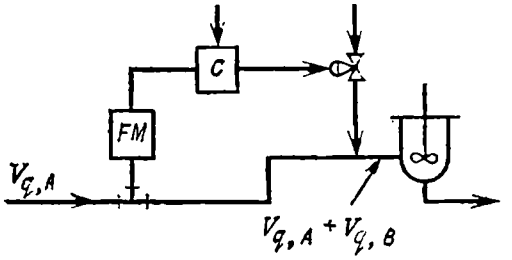

Fig. VI-27. Measurement of controlled stream and application of control action to manipulated stream
FM — flow-rate meter; *C* — controller

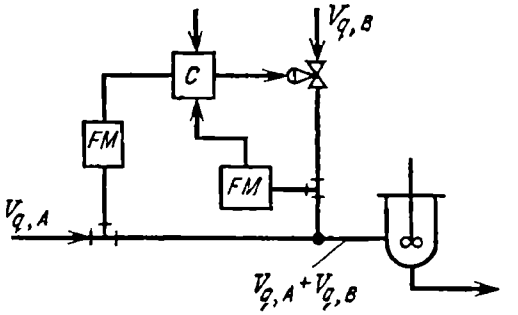

Fig. VI-28. Measurement of two streams and feedback control
FM — flow-rate meter; *C* — controller

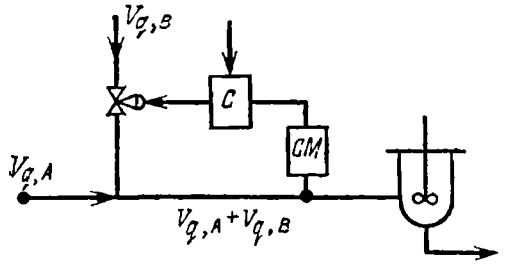

Fig. VI-29. Direct ratio control
C — controller; *CM* — concentration meter

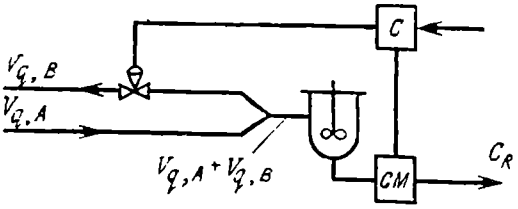

Fig. VI-30. Ratio control and yield measurement
C — controller; *CM* — concentration meter

Figure VI-29 illustrates direct control of the reactant flow rate ratio. In this case, a concentration meter, CM, measures the concentration of reactant A or B or both in the controlled stream. Its signal is then applied to a controller which operates the control valve on the line carrying the manipulated stream. In this way, by manipulating $V_{q,B}$, the concentrations c_A and c_B can be controlled in the leaving stream. This is an example of direct composition control with feedback.

Figure VI-30 shows a system to control the ratio of reactant flow rates through measurement of product concentration, c_R, in the leaving stream.

Control by manipulation of the flow rate and temperature of the heat-transfer medium. As an example, we shall take up control of catalytic

reactors. The choice of a particular scheme depends on the arrangement of the process to be controlled. For example, temperature and fractional conversion in adiabatic reactors may be controlled in any one of three ways: (1) by installing intermediate heat exchangers between catalyst beds; (2) by injecting a cold fluid between the beds; or (3) by injecting a cold inert gas between the beds.

We take the oxidation of SO_2 to SO_3, which is a reversible exothermic reaction, as an example, and plot on the *x-vs-t* coordinates (Figs. VI-32 through VI-34) the curves corresponding to the equilibrium fractional conversion. As a result, we obtain straight-line segments relating fractional conversion and temperature for an adiabatic reactor (see p. 320).

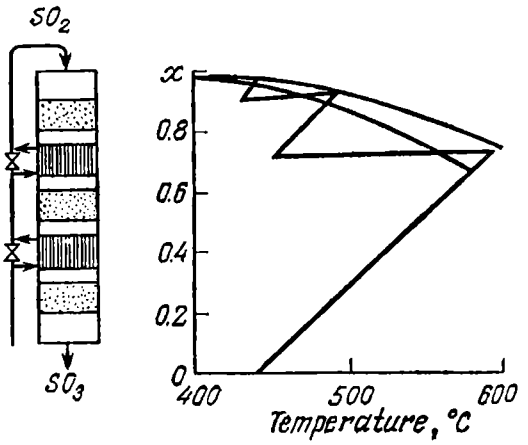

Fig. VI-31. Temperature control in an adiabatic reactor with intermediate heat exchangers

The effect of intermediate heat exchangers installed between catalyst beds is illustrated in Fig. VI-31 where the horizontal straight-line segments apply to operation of the heat exchangers, and the slant lines, to changes in the fractional conversion from stage to stage.

With the final fractional conversion and the number of stages specified in advance, changes in the fractional conversion and temperature may be distributed between the catalyst stages in several ways.[8] The best distribution of temperature and fractional conversion between stages should satisfy the condition

$$V_c = \sum V_i = \text{minimum}$$

where V_c is the total catalyst volume in the reacting apparatus, and V_i is the catalyst volume in an *i*th stage.

The initial temperature, t_{i0}, of the gas entering the catalyst bed and the final fractional conversion, x_{if}, in an *i*th stage may be varied in any arbitrary manner. According to the condition of minimization, we have

$$\delta V_c = \frac{\partial V_1}{\partial x_{1f}}\delta x_{1f} + \frac{\partial V_1}{\partial t_{10}}\delta t_{10} + \frac{\partial V_2}{\partial x_{1f}}\delta x_{1f} + \frac{\partial V_2}{\partial x_{2f}}\delta x_{2f} + \frac{\partial V_2}{\partial t_{20}}\delta t_{20} + \frac{\partial V_3}{\partial x_{2f}}\delta x_{2f} + \frac{\partial V_3}{\partial x}\delta x_{3f} + \frac{\partial V_3}{\partial t_{30}}\delta t_{30} + \ldots + \frac{\partial V_n}{\partial x_{n-1,f}}\delta x_{n-1,f} + \frac{\partial V_n}{\partial x_{n-1,f}} = 0 \quad \text{(VI-44)}$$

whence

$$\frac{\partial V_1}{\partial x_{1f}} = \frac{\partial V_2}{\partial x_{1f}} = \frac{\partial V_2}{\partial x_{2f}} = \ldots = \frac{\partial V_{n-1}}{\partial x_{n-1,f}} + \frac{\partial V_n}{\partial x_{n-1,f}} = 0 \quad \text{(VI-45)}$$

$$\frac{\partial V_1}{\partial t_{10}} = \frac{\partial V_2}{\partial t_{20}} = \ldots = \frac{\partial V_n}{\partial t_{10}} = 0 \quad \text{(VI-46)}$$

With $2n-1$ equations, we can define $2n-1$ quantities, namely $(n-1)$ values of x_{if} and n values of t_{i0}. The temperature past an ith catalyst stage, t_{if}, is defined as

$$t_{if} - t_{i0} = T_a(x_{if} - x_{i0}) \qquad \text{(VI-47)}$$

where T_a is the maximum rise in the gas temperature corresponding to changes in fractional conversion from 0 to 1 under adiabatic conditions.

The catalyst volume per stage is given by

$$V_i = V_q \tau_i = V_q \int_{x_{i-1,f}}^{x_{if}} \frac{\partial \tau}{\partial x}\, dx \qquad \text{(VI-48)}$$

where τ_i is an arbitrary contacting time.

The above relationships may also be utilized to select optimum operating conditions for reactors already in use. In designing new reactors, the final fractional conversion is specified in advance, and an optimum catalyst distribution is sought. With reactors already in use, the reaction rate constants are deduced from the actual values of fractional conversion, temperature and catalyst charge, and conditions are then found that will correspond to the highest final conversion. In such cases, only the initial gas temperature ahead of catalyst stages may be changed at will. Therefore, the condition for a maximum final fractional conversion is defined as

$$\partial x_{nf}/\partial t_{i0} = 0 \qquad \text{(VI-49)}$$

where $i = 1, 2, \ldots, n$.

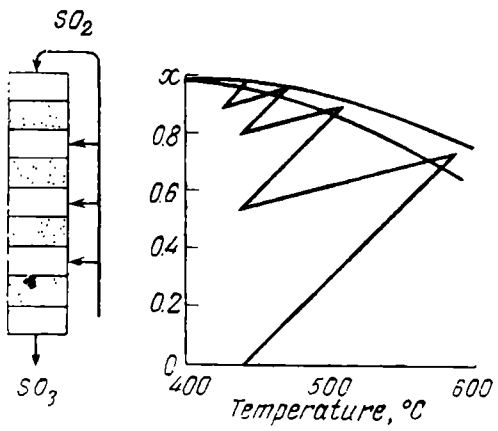

Fig. VI-32. Temperature control in an adiabatic reactor by injection of feed between beds

A similar approach may be used in finding optimum operating conditions for other process schemes. For example, as already noted, the temperature ahead of catalyst stages may be controlled by adding some fresh feed (Fig. VI-32). In contrast to the previous case, the addition of fresh feed brings down the fractional conversion ahead of the catalyst bed, while the volume of the gas passing through the bed increases. In the *t-vs-x* plot, the lines representing the cooling of the gas between catalyst stages are slant.

As with intermediate heat exchangers, the desired operating conditions are secured by adjusting the initial temperature of the gas and the final fractional conversion. However, any change in the initial temperature ahead of the catalyst bed entails a change in the distribution of the bulk gas between stages. Therefore, the catalyst volume in each stage is of necessity a function of the initial temperatures of all stages, and Eq. (VI-46) has to be replaced with an equation of the form

$$\partial V/\partial t_{i0} = 0 \qquad \text{(VI-50)}$$

When the gas between the beds of contact mass is cooled by adding more fresh feed, the added cold gas reacts in the presence of the reaction products. Since the reaction rate decreases with increasing fractional conversion, the needed catalyst volume is markedly greater than that for an apparatus with intermediate heat exchange.

In comparison with the above method, it appears more advantageous to reduce the temperature of the gas between catalyst stages by injecting a reaction component for which a complete conversion is not mandatory. In sulphuric-acid contactors, this purpose is served by cold air (Fig. VI-33). Each time an amount of air is added to the contactor, the SO_2 concentration falls, entailing appropriate changes in the equilibrium fractional conversion and in the slope of the adiabat defining the warm-up of the gas. In the *t-vs-x* plot, the lines representing the cooling process are parallel to the *x*-axis, and the slope of the adiabates increases from stage to stage. The ordinates of the equilibrium and optimum temperature curves are shifted upwards with increasing stage No.

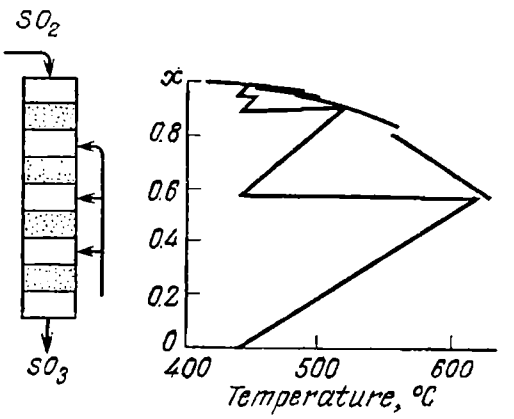

Fig. VI-33. Temperature control in an adiabatic reactor by injection of an inert cold gas between beds

Changes in the amount of catalyst per stage make it necessary to adjust the gas temperature at the inlet to, and the fractional conversion at the exit from, each stage. From the condition for a minimum of the total amount of catalyst, the following equations may be derived:

$$\frac{\partial V_1}{\partial x_{1f}} + \frac{\partial V_2}{\partial x_{1f}} = \frac{\partial V_2}{\partial x_{2f}} + \frac{\partial V_3}{\partial x_{2f}} = \ldots = \frac{\partial V_{n-1}}{\partial x_{n-1,f}} + \frac{\partial V_n}{\partial x_{n-1,f}} = 0 \quad \text{(VI-51)}$$

$$\frac{\partial (V_1 + \ldots + V_n)}{\partial t_{10}} = \frac{\partial (V_2 + \ldots + V_n)}{\partial t_{20}} = \ldots = \frac{\partial V_n}{\partial t_{n0}} = 0 \quad \text{(VI-52)}$$

To these equations must be added those used to find the amount of air added, the concentrations of reactants, equilibrium fractional conversion, contacting times, and gas temperature at exit from each stage. With the initial and final fractional conversions, initial concentration and initial gas volume specified in advance, the calculation of optimum operating conditions for a five-stage contacting unit cooled by cold air involves the use of 31 equations. These equations can be solved readily and in a variety of combinations on a digital computer.

In *reacting apparatus with intermediate heat exchange*,[8] the process has to be broken off on each stage at a certain fractional conversion controlled by the maximum safe warm-up of the catalyst. Therefore, the temperature of such an adiabatic bed is extremely sensitive to input conditions (feed temperature, flow and concentration). Thus, for the oxidation of methanol,

the parametric sensitivity of the temperature at the exit from the bed, $t_f K$, to the inlet temperature, t_i, is $dt_f/dt_i \approx 4.5$.

If a temperature disturbance is not damped after each stage, it will progressively build up from stage to stage. To damp or at least moderate such a disturbance after one catalyst stage and prevent it from propagating throughout the apparatus, it is desirable to effect intermediate cooling in heat exchangers with an external heat-transfer medium; then the disturbance can be damped by providing an extra surface area. In other cases, special methods have to be used to stabilize operating conditions in each stage.

Intermediate heat exchangers are capable of dealing with departures from operating conditions in all stages, except the last one. In order that the parametric sensitivity of the last stage be kept low, the reaction in it must be carried to completion. The required number of adiabatic catalyst stages for an apparatus with intermediate heat exchange must be equal to the ratio of the adiabatic temperature rise, ΔT_a, to the temperature range of the catalyst, ΔT_c. In contrast to units with internal heat exchange, reactors with intermediate heat exchange are simpler mechanically, have as a rule a smaller heat transfer surface area, are more convenient to install, and provide for a more uniform distribution of the reaction mixture over the catalyst.

These features of units with intermediate heat exchange prove very valuable in large-capacity plants. The accompanying increase in the complexity of the associated automatic control system is of minor consequence.

Units with intermediate heat exchange are well adapted to reversible exothermic reactions. In such reactions the equilibrium fractional conversion decreases with rising temperature. Therefore, it is likely that an equilibrium fractional conversion is reached at the exit from each adiabatic catalyst stage. If so, the parametric sensitivity of each stage must be low, and practically any number of catalyst stages may be used. Inter-stage cooling, too, may be arranged in any applicable manner (in the form of heat exchangers, by addition of cold reaction stock or a gas of another initial composition, by use of an external heat-transfer medium in intermediate heat exchangers, or by use of the reaction stock as a heat-transfer medium).

To sum up, reacting units with intermediate heat exchange are well adapted to: (1) reversible exothermic processes; (2) use of intermediate heat exchangers with an external heat-transfer medium; (3) processes in which the fractional conversion in the last stage is close to its maximum value; and (4) large-scale manufactures.

In apparatus with internal heat exchange, the heat generated by the process is removed from the reaction zone through a heat-transfer surface at the same rate. Therefore, units with internal heat exchange are compact in layout and small in size. However, in order to remove enough heat, a sufficiently large surface should be fitted inside the catalyst bed. Because of this, reactors with internal exchange are usually tubular units. In effect, a single contacting unit is a combination of a large number (up to several thousand) of small units (tubes) operating in parallel.

If the process is to proceed normally, it is essential that all tubes operate as one. As a rule, however, the tubes are not properly sized as to diameter or wall thickness, nor is it possible to pack each tube with an equal amount of catalyst. Obviously, the distribution of the feed between the tubes may be anything but uniform, and they inevitably operate in a somewhat different manner.

Reactor control is impeded, too: the temperature is a maximum inside the catalyst bed, and precisely this area has the highest parametric sensitivity, or is the "danger spot" in the reactor. Any instruments introduced into the slim reactor tubes will immediately change the flow pattern there and upset the operating conditions of the catalyst bed. As a consequence, the sensors will give indications of temperature different from that in the unmonitored tubes. A further complication in this case is that any change in operating conditions of the reactor brings about a shift in the position of the maximum temperature region inside the catalyst bed.

In units with internal heat exchange, the rate of heat removal is almost constant with tube length, while the rate of reaction and, as a consequence, the rate of heat generation vary considerably with the progress of the reaction, especially if the reaction is carried to the complete depletion of reactants. It is not unlikely, therefore, that the catalyst closer to the exit end might be cooled and the reaction might slow down. To avoid this, resort is made to units utilizing a combination of intermediate and internal heat exchange. In these units, chemical change at the final stages proceeds adiabatically or, better still, with a rise in temperature. The operating conditions of the catalyst bed in all tubes are likewise rendered more uniform (there is less short-circuiting of gas, a more equal fractional conversion in the various tubes, etc.). Unfortunately, units with combination heat exchange share the difficulties of control with units utilizing internal heat exchange.

Stability of the controlled reactor and heat removal system. Control of heat removal from reactors must be tied in with their thermal stability.[12]

The total heat removed by a heat-transfer medium is given by

$$Q_m = KF(T - T_m) \qquad \text{(VI-53)}$$

where T is the bed temperature, T_m is the average (or, rather, the logarithmic mean) temperature of the heat-transfer medium, F is the heat-transfer surface area, and K is the heat-transfer coefficient.

When a process is analysed for thermal stability, it is assumed that T_m is an external unvarying factor, and the derivative of heat removal with respect to bed temperature is defined as

$$dQ_m/dT = KF \qquad \text{(VI-54)}$$

When a reactor is analysed for thermal stability, with allowance for changes in the temperature of the heat-transfer medium, T_m, we have

$$dQ_m/dT = KF(1 - dT_m/dT) \qquad \text{(VI-55)}$$

As T rises, heat removal increases, and the temperature of the heat-

transfer medium, T_m, rises, too, if its feed rate is held constant. In other words, $dT_m/dT > 0$, and the derivative dQ_m/dT evaluated from Eq. (VI-55) decreases.

Thus, the slope of the actual relationship $Q_m = (T)$ for the reactor turns out to be more gradual than is assumed in analysis of the process and, as a consequence, the thermal stability region for the reactor is narrower in comparison with that of the chemical process.

In the discussion that follows, four typical heat removal systems are examined, with special emphasis on the effects that they have on the stability of the associated controlled system. Differences in the stability conditions are brought out between process analysis and system analysis, and appropriate recommendations for control are given.

Systems with a single-phase heat-transfer medium. In this case, heat removal is controlled by manipulating the flow rate of the heat-transfer medium. A practical example of such a system is an apparatus with an internal heat exchanger, provided that at the exit from the heat exchanger the medium is not raised to its boiling point even under the most adverse conditions.

From the view-point of process control, this system is unsatisfactory, because the heat exchanger is a distributed-capacitance element, which introduces a considerable time lag in the plant's response to the control (corrective) action. In contrast, disturbances act directly on the "process" block of the system, whose response is like that of a single-capacitance element, if the reactor operates under conditions of complete mixing.

Systems with partial vaporization of the heat-transfer medium. In these systems, heat removal is controlled by manipulating the vapour pressure of the heat-transfer medium and, as a consequence, the temperature of the vapour-liquid mixture and the vaporizer.

In such heat removal systems, vaporizer pressure is controled by admitting a secondary heat-transfer medium (most often, water) into the condenser. The internal space of the vaporizer-condenser system is filled with condensate to a level such that in any duty the vaporizer will supply a vapour-liquid mixture.

Relative changes in the temperature of the vapour-liquid mixture, that is, of the primary heat-transfer medium, T_m, and in the amount of condensed vapour are the internal system parameters, while the external factors remain, as before, relative changes in feed, rate feed temperature, initial temperature and flow rate of the secondary heat-transfer medium.

If the bed temperature rises while the flow rate of the secondary heat-transfer medium is held constant, the pressure and temperature of the vapour-liquid mixture in the vaporizer will rise too, and this will (as already explained) result in a narrower stability region of the reactor in comparison with that of the process proper.

Systems with total vaporization of the heat-transfer medium. Here, heat removal is controlled by manipulating the level of the vapour-liquid mixture in the vaporizer, that is, by manipulating the effective surface area of heat transfer. The mixture level is manipulated by controlling the flow rate of

condensate to be vaporized to the vaporizer. Physically, a total-vaporization heat-removal system may be similar to that with a single-phase heat-transfer medium examined above, but its operating conditions must be chosen so that under any duty all of the condensate admitted will be fully vaporized within the vaporizer.

Should the original heat balance be upset, the system will be unable to reach a new equilibrium state in which the vaporization of the same amount of condensate at the same initial temperature and pressure in the system can raise heat removal. Thus, total-vaporization heat-removal systems operate practically always under unsteady-state conditions.

However, total-vaporization systems are easy to control owing to their specific dynamic behaviour. The point is that the vapour-liquid mixture in the vaporizer undergoes "swelling". This swelling, that is, a rise in the level of the vapour-liquid mixture and, as a consequence, an increase in the effective surface area of heat transfer are caused by a rise in the bed temperature and the accompanying increase in the heat flux which leads to an increased moisture content of the vapour-liquid mixture. As a result, the system shows a better self-regulation. Unfortunately, this self-regulation is short-lived. With time the material balance around the vaporizer is upset, all of the heat-transfer medium it holds is vaporized, the mixture level drops, and the effective surface area of heat transfer slowly decreases.

Heat-removal systems with total vaporization of water. These systems have found successful application in the oxidation of naphthalene to phthalic anhydride in a fluidized catalyst bed reactor and also in the oxidation of benzene to maleic anhydride (unstable processes in both cases).

Systems without a heat-transfer agent. The reactor is cooled, that is, heat removal is effected, by heating the stock admitted to the reactor. Control is effected by manipulating the feed inlet temperature by, say, varying the ratio of the flow rates of the heated and unheated streams.

Changes in the temperature conditions of the process will not directly affect the feed temperature, if the feed is preheated externally rather than regeneratively. Under such constraints, the initial feed temperature, T_0, may be treated as an independent external variable, and the stability condition for the plant as a whole is the same as for the process proper.

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CHAPTER VII

ANALYSIS AND SYNTHESIS OF CHEMICAL ENGINEERING SYSTEMS

In Chapter I, we examined the hierarchy of chemical manufacture in general terms. The succeeding chapters dealt with the principles of cybernetic analysis of unit operations and processes of chemical engineering at the lower level of this hierarchy.

This chapter will be devoted to cybernetic analysis and synthesis of a collection of processes that make up the process entity at the second level of the hierarchy—the departmental level of a chemical factory.

At the first level of the hierarchy, the objective is to find optimum operating conditions for individual units. At the second level, where the optimum of one unit may well affect that of another within the same line, the objective in the synthesis of chemical-engineering systems from unit processes is to optimize operating conditions for the entire line on the basis of a common goal.

Thus, a *chemical-engineering system* is an ordered assemblage of units, or elements, interconnected by process flows and operating towards a common goal; these elements carry out chemical-engineering processes which involve three basic operations—preparation of the feed, chemical change proper, and recovery of wanted products. Accordingly, an element of a chemical-engineering system may be defined as that which carries out a specific chemical-engineering process.

For the purpose of analysis and synthesis, a unit process may be looked upon as a *process operator* which brings about a qualitative or a quantitative change in the material and energy streams of the system.[1]

The basic process operators of chemical engineering (Fig. VII-1*a*, *b* and *c*) are the mixing operator, the chemical-change operator, and the separation operator. These three operators form the basis of any chemical-engineering process. Besides, a chemical-engineering system may include *auxiliary operators* to effect heating (cooling) and compression (expansion) (Fig. VII-1*d* and *e*).

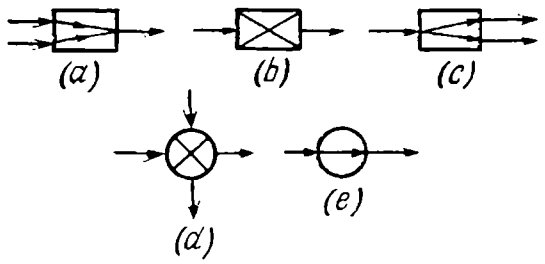

Fig. VII-1. Chemical-engineering operators
(*a*) mixing operator; (*b*) chemical-change operator; (*c*) separation operator; (*d*) heating (cooling) operator; (*e*) compression (expansion) operator

In the synthesis of any chemical manufacture, the following flows may be utilized as *process links* between the component units: a *series flow* (Fig. VII-2*a*), such as used in unitized systems (for example, in the manufacture of ammonia) and also in cases where it is sought to enhance the efficiency of a particular process operator (for example, where a higher fractional conversion is desired); a *parallel flow* (Fig. VII-2*b*), employed in cases where it is sought to increase the throughput of a system or where it is desired to make two sub-products, *A* and *B*, for the manufacture of one end product, *C*; a *return flow*, or *recycle* (Fig. VII-2*c*), used for a better utilization of source materials or energy, and also for the purpose of regeneration;

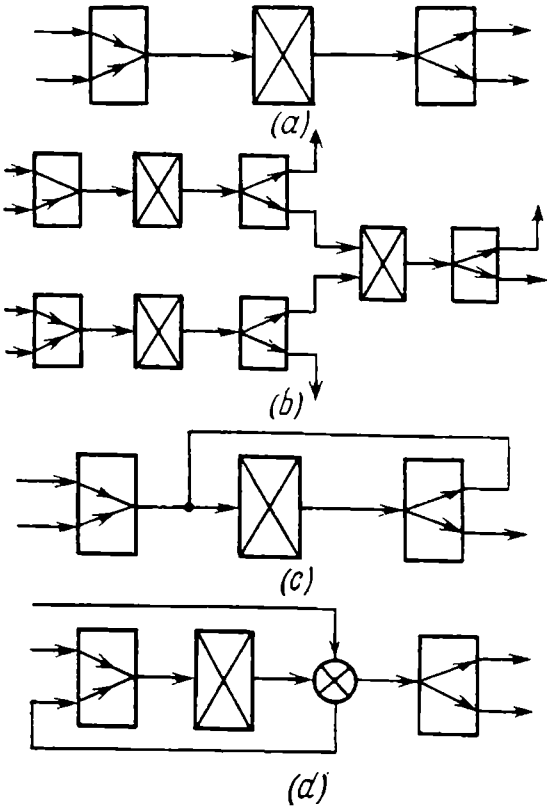

Fig. VII-2. Chemical-engineering system with (*a*) series; (*b*) parallel; (*c*) return or recycle and (*d*) cross flows

and a *cross flow* (Fig. VII-2*d*) used to enhance the utilization of energy in a system.

The overall task that faces an investigator in the field of chemical-engineering systems may be divided into two stages:

(a) analysis of complex chemical-engineering systems;

(b) synthesis of chemical-engineering systems.

In synthesis of a chemical manufacture, two situations may arise:

(1) Chemical-engineering processes and units are specified in advance and an optimum process layout is to be selected from a variety of possible combinations. In such a case, each component process is given by specifying only its input and output variables, without a detailed mathematical description. With this approach, the various processes may be linked together by combining the respective information flows and an idea formed about the properties of the system as a whole.

(2) The process layout is specified in advance, and applicable processes and units are to be selected and their operating conditions optimized.

In both situations, the designer is assumed to have a mathematical model of the chemical-engineering system.

A computational procedure that may be involved in the analysis, synthesis and optimization of a chemical-engineering system may be carried out in the following three basic steps:

Step one. The functional relationships of the system are analysed so as to decompose the system into sub-systems (that is, into individual units or sets of units). Optimum sequences are found for sub-system computation and the least possible number of recycle variables for recycle sub-systems is determined, so that the number of dimensions involved and the labour required in solving the problem may safely be reduced.

Step two. Efficient and simple iterative procedures are developed in order to determine the material and energy flows of the chemical-engineering system from its recycle variables.

Step three. All computational and preliminary work is optimized on a computer.

As is seen, major difficulties in the mathematical modeling, analysis and synthesis of complex chemical-engineering systems are the multi-dimensional character of problems, the associated need to resolve such systems into simpler sub-systems, and also the mathematical description of the component processes.

The symbolic (mathematical) model of an *i*th process operator may be defined as

$$[Y^i_{m1}] = [F^i_{mn}\{[X^i_{n1}], [K^i_{p1}]\}] \qquad \text{(VII-1)}$$

where $[X^i_{n1}]$ is the vector of the input process flow variables; $[Y^i_{m1}]$ is the vector of the output process flow variables; $[K^i_{p1}]$ is the vector of the element design variables; $[F^i_{mn}\{\ \}]$ is a non-linear vector function; $n(m)$ is the number of input (output) process flow variables; p is the number of design variables of an *i*th element.

For each element of a chemical-engineering system, the functional relationship, Eq. (VII-1), is, as a rule, a set of multidimensional non-linear algebraic or differential equations whose solution would take a lot of time even on a digital computer. This is why, at the early stages of design work, it is sought to develop simpler mathematical models just sufficient to describe faithfully the physical and chemical processes in the element. At the final stages of design work, it is important to use more accurate and therefore more complex mathematical models that can give a fuller account of the process kinetics and a more realistic picture of how the process and element variables may affect the performance of the system as a whole.

Simple mathematical models for elements can be built by use of linearization functions, approximations, experiment designs involving a complex mathematical model developed from standard chemical-engineering models, and also by approximation of distributed-parameter elements with lumped-parameter ones.

If the vector function $[F^j_{mn}]$ for a jth element of a chemical-engineering system in Eq. (VII-1) is a linear function of the vector of input flow variables, $[X^j_{n1}]$, the mathematical model of the element may be written as

$$[Y^j_{m1}] = [R^j_{mn}] \times [X^j_{n1}] \qquad \text{(VII-2)}$$

where $[R^j_{mn}]$ is the transformation matrix of the jth element and $m(n)$ is the number of output (input) flow variables.

Each element Γ_{mn} of the transformation matrix $[R_{mn}]$ is a coefficient of the functional relationship, whose value is independent of the input-flow variables.

Depending on the form of the transformation matrix $[R_{mn}]$, three elements may be singled out in a chemical-engineering system, namely: flow splitters, flow separators, and reactors.

For each jth output flow, the transformation matrix of a flow splitter is a diagonal matrix such that $\Gamma_{11} = \Gamma_{22} = \ldots = \Gamma_{nn} = a = \text{constant}$, namely:

$$[R^*_{nn}] = a \times [E_{nn}] \qquad \text{(VII-3)}$$

where $[E_{nn}]$ is the unit matrix.

The functional relationship, Eq. (VII-2), for a flow splitter has the form:

$$[Y_{n1(j)}] = a \times [E_{nn}] \times [X_{n1}] \qquad \text{(VII-4)}$$

For a flow separator, the functional relationship between the vectors $[Y_{m1}]$ and $[X_{m1}]$ may be stated as

$$[Y_{m1(j)}] = \begin{bmatrix} \Gamma_{11} & 0 & \ldots & 0 \\ 0 & \Gamma_{22} & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & \ldots & \Gamma_{mm} \end{bmatrix} \times [X_{m1}] \qquad \text{(VII-5)}$$

where the matrix elements Γ_{mm} are not the same; they are different functions of the variables of a chemical-engineering element.

If a reactor carries out z independent reactions at a time, the material balances on the various reaction components may be written as

$$\sum_{j=1}^{k} \nu_{ij} M_j = 0 \qquad \text{(VII-6)}$$

where ν_{ij} is the stoichiometric coefficient of a jth component in an ith reaction, M_j is the molecular mass of the jth component, $i = 1, 2, 3, \ldots, z$ is the number of independent reactions, and $j = 1, 2, 3, \ldots, k$ is the number of reaction components.

The stoichiometry matrix $[S]$ for Eqs. (VII-6) has the form

$$[S] = \begin{bmatrix} \nu_{11} & \ldots & \nu_{1k} \\ \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots \\ \nu_{z1} & \ldots & \nu_{zk} \end{bmatrix} \qquad \text{(VII-7)}$$

The functional relationship between the vectors of input and output process flow variables of a reactor may be written as

$$[Y] = ([E] + [C] \times [S]) \times [X] \qquad \text{(VII-8)}$$

where $[E]$ is the unit matrix, $[C]$ is the rate constants matrix, and $([E] + [C] \times [S]) = [R]$ is the transformation matrix of the reactor.

The matrix $[R]$ is non-diagonal, its elements being dependent on the variables of the chemical-engineering element.

For distributed-parameter chemical-engineering elements which include vessels carrying out countercurrent mass-transfer processes, the relationship coefficients, that is the transformation matrix elements, are determined by the reduction of a zone cascade mathematical model along a spatial coordinate and its linearization within the range of values of the input flow vector. Reduction of a mathematical model is also resorted to when chemical-engineering processes are calculated on the basis of average driving forces or equilibrium relations.

The elements of transformation matrices are estimated by the method of experimental design, using a standard mathematical model developed from studies into the physical and chemical aspects of the process in question. By employing full experimental designs and their fractional replicates for model testing, the designer can materially reduce the amount of computational work involved and obtain sufficiently accurate results in the desired range of changes in the input process flow vector.

With chemical-engineering elements for which mathematical models are essentially nonlinear, piecewise linear approximation has to be used in order to obtain a transformation matrix for each linear portion separately. In such cases, the elements of transformation matrices are varying quantities.

The presentation of symbolic (mathematical) models of chemical-engineering elements in transformation matrix form (Eq. VII-2) greatly simplifies the analysis, synthesis and optimization of complex chemical-engineering systems. This is because the number of dimensions involved is reduced, the problems become less complicated mathematically, and non-iterative procedures can be employed for calculations.

Studies of a complete chemical-engineering system involve the use of a complete mathematical model of that system. Such a model is developed by adding to the equations describing the individual elements, like Eq. (VII-1), the constraint equations that describe the internal structure of the system.

The following topological models may be used in the analysis and synthesis of chemical-engineering systems.

Above all, these are flow graphs and structural graphs which depict the process topology of a system and establish direct relationships between changes in the process topology and the quantitative characteristics of that system.

A second class of topological models are information-flow multigraphs and information graphs. These graphs bring out the specific features of the symbolic (mathematical) models used and allow an optimum strategy to be worked out for the analysis of the system in question.

A third class of topological models includes signal flow graphs which show the functional relationships between the variables of a symbolic (mathematical) model. Signal flow graphs may be used to analyse the dynamic and static behaviour of chemical-engineering system, to calculate the sensitivity of a system to changes in system variables and to test systems for process stability.

VII-1. CALCULATION OF MATERIAL AND ENERGY BALANCES FOR CHEMICAL ENGINEERING SYSTEMS

In developing balance equations, it is assumed that the system is in a steady state and has a finite set of elements, while the elements interact with one another and the system does so with the surroundings through a finite set of physical flows.

The properties of an ith physical flow can be described by a π_i set of variables of state:

$$\pi_i = \{m_i, x_{i1}, x_{i2}, \ldots, x_{ik}, t_i, P_i, H_i\} \qquad \text{(VII-9)}$$

where m_i is the total mass flow rate of a material, x_{ik} is the fraction of the kth reaction component, t_i is the temperature, P_i is the pressure, and H_i is the heat flow rate in the ith physical flow.

The parameter number, π_i, of a physical flow is equal to the cardinality of the applicable set of variables of state.

On the basis of the laws of conservation of mass and energy, a set of balance equations may be developed for each ith element (sub-system) of a

chemical-engineering system, which will include the following independent equations:

(a) a material balance on the overall mass flow rate of physical flows:

$$\sum_{j=1}^{n} m_{ji} = 0 \qquad \text{(VII-10)}$$

(b) a material balance on the mass flow rate of components (which may be chemical elements or free radicals) in physical and fictitious flows:

$$\sum_{j=1}^{n} m_{ji}X_{jk} + \sum_{e=1}^{v} G_e^* = 0 \qquad \text{(VII-11)}$$

where G_e^* is the fictitious material flow defining the quantity of a component reacted or formed by a reaction;

(c) a heat balance on the heat flow rate of physical and fictitious heat flows:

$$\sum_{j=1}^{n} m_{ji}h_j + \sum_{e=1}^{v_1} Q_e^* = 0 \qquad \text{(VII-12}a\text{)}$$

or

$$\sum_{j=1}^{n} m_{ji}\bar{C}_j t_j + \sum_{e=1}^{v_1} Q_e^* = 0 \qquad \text{(VII-12}b\text{)}$$

where $j = 1, n$ is the number of physical flows related to the ith element, m_{ji} is the total mass flow rate of a material, X_{jk} is the fraction of the kth component per unit of total mass flow rate of a material, h_j is the enthalpy, $\bar{C}_j$ is the average specific heat, t_j is the temperature, and Q_e^* is the heat flow rate of the eth fictitious heat flow, corresponding to the heat generated or absorbed by the physical and chemical changes that take place in the system element.

In the general case, the balance equations, Eqs. (VII-10) through (VII-12), make up a set of nonlinear equations. However, on making certain assumptions, the balance equations of any chemical-engineering system may be reduced to a linear form:

(a) if the variables m_{ji} are specified, the balance equations are linear in the variables X_{jk} and $h_j(t_j)$;
(b) if the variables X_{jk} and/or h_j are specified, the balance equations are linear in the variables m_{ji}. (VII-13)

The balance equations may be reduced to a linear form, using the concept of generalized flows. Each πth element (sub-system) of a system may be described by a linear balance equation of each type of generalized flows:

$$\sum_{j=1}^{n} W_{ji} = 0 \qquad \text{(VII-14}a\text{)}$$

or

$$\sum_{j=1}^{k} W'_{ji} + \sum_{j=1}^{v} W^{*}_{ji} = \sum_{j=1}^{n} W''_{ij} + \sum_{j=1}^{e} W^{**}_{ij} \qquad \text{(VII-14}b\text{)}$$

The independent equations of the form (VII-12) developed for all system elements, tailored to the process topology of the system, make up a set of linear balance equations of one type of generalized flows, applicable to the system as a whole:

$$[A] \times [W] = 0 \qquad \text{(VII-15)}$$

where $[A] = [a_{ij}]$ is the matrix of balance equations, such that

$$\left.\begin{array}{ll} a_{ij} = +1 & \text{if the } j\text{th generalized flow enters the } i\text{th element;} \\ a_{ij} = 0 & \text{if the generalized flow is not linked to a system element;} \\ a_{ij} = -1 & \text{if the generalized flow leaves the element:} \end{array}\right\} \qquad \text{(VII-16)}$$

$[W] = [W_{j1}]$ is the column matrix of one type of generalized flows, $i = 1, 2, 3, \ldots, k$ is the number of system elements and $j = 1, 2, 3, \ldots, e$ is the number of generalized flows.

In order to determine material and thermal loads on system elements, the balance equations for one type of generalized flows, Eqs. (VII-15), should be extended to include constraint equations. These equations describe the physical and chemical aspects of the process (or processes) occurring in the system. Constraint equations fix the component composition of the total physical flows, the size of sources (sinks) of reaction components, the size of the heat sources (sinks) of the respective physical and chemical changes, stoichiometric relations between reaction components, interrelations between flows when the coefficients in the transformation matrices of elements are known, the dependence of flow magnitudes on specified process variables, the output of the system in terms of products, etc.

In the general case, constraint equations are implicit functions of many variables:

$$F_i(\pi_i, \gamma_i, \alpha, \nu, K, D) = 0 \qquad \text{(VII-17)}$$

where π_i defines the variables of state of the physical flows, γ_i defines the constraint coefficients or the efficiency of the system elements, α defines the molal ratios of the reaction components, ν represents the stoichiometric coefficients and physico-chemical constants, K represents the design and process variables of the system elements, and D defines the operating conditions for the system.

The independent generalized-flow balance and constraint equations of a chemical-engineering system may be written in the following general matrix form

$$\begin{bmatrix} A_{k\times e_1} & 0 & 0 & 0 \\ 0 & A_{k_1\times e_2} & 0 & 0 \\ 0 & 0 & A_{k_2\times e_3} & 0 \\ 0 & 0 & 0 & E_{k_3\times k_3} \end{bmatrix} \times \begin{bmatrix} \mu_{e_1\times 1} \\ \mu_{e_2\times 1} \\ Q_{e_3\times 1} \\ F_{k_3\times 1} \end{bmatrix} = 0 \qquad \text{(VII-18)}$$

where

$[\mu_{e_1\times 1}]$, $[\mu_{e_2\times 1}]$, $[Q_{e_3\times 1}]$ = column submatrices of the system's generalized flows, deduced from the equation

$$W_{ji} = m_i X_\pi (X_\pi \in \pi_i)$$

$[F_{k_3\times 1}]$ = column submatrix whose elements correspond to the left-hand sides of the constraint equations, Eq. (VII-17);

$[A_{k_1\times e_1}]$, $[A_{k_1\times e_2}]$, $[A_{k_2\times e_3}]$ = submatrices with elements a_{ij} deduced from Eq. (VII-16);

$[E_{k_3\times k_3}]$ = unit submatrix;

k = number of elements (sub-systems) in the system;

k_1 = number of balance equations for generalized flows of the type W_{2i} and W_{3i};

k_2 = number of balance equations for generalized flows of the type W'_{3i} and W''_{3i};

k_3 = number of constraint equations;

e_1 = number of generalized flows of the type W_{1i};

e_2 = number of generalized flows of the type W_{2i} and W_{3i};

e_3 = number of generalized flows of the type W'_{3i} and W''_{3i}.

In the above notation:

$$W_{1i} = m_i;$$

$$W_{2i} = \begin{cases} W'_{2i} = m_{ki} = m_i \times X_{ik} \\ W''_{2i} = G_i^* \end{cases}$$

$$W_{3i} = \begin{cases} W'_{3i} = \begin{cases} q_i = m_i \times h_i \\ q_i = m_i \times \bar{C}_i \times t_i \end{cases} \\ W''_{3i} = Q_i^* \end{cases}$$

With chemical-engineering systems having $k < 3$ elements, no difficulties are experienced in developing balance equations, in selecting free information variables, or in solving the balance matrix, Eq. (VII-18). With $k > 3$, however, the difficulties are considerable, because one is forced to make a "happy choice" of free information variables. Otherwise, a large number

of iterations will have to be made and all sets of free information variables will have to be tried before the balance matrix, Eq. (VII-18), can be solved.

One of the noniterative procedures for solving the balance matrix for complex chemical-engineering systems is based on the concept of a flow graph which is isomorphous with the system under study and gives a true representation of the process streams in the system.

The flow graph of a chemical-engineering system

$$G = G(A) = (A, T)$$

is shown in Fig. VII-3.

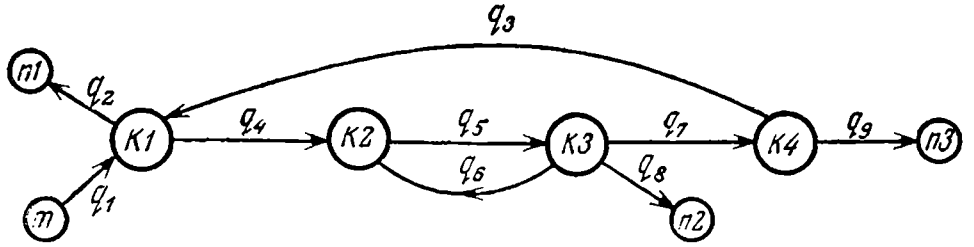

Fig. VII-3. Flow graph of a chemical-engineering system

The nodes, $G(A)$, of the graph represent the units of the system, and the arcs, (T), represent the flows. This flow graph may be described by a material (or energy) balance matrix of the form

$$[A] \times [Q] = 0 \qquad \text{(VII-19)}$$

where Q = column matrix with e elements in the form of material (or energy) flows;
A = matrix of order $(k \times e)$ with elements such that:
$a_{ij} = 0$ if the ith flow is not linked to the jth unit;
$a_{ij} = +1$ if the ith flow enters the jth unit;
$a_{ij} = -1$ if the ith flow leaves the jth unit.

Using the topological properties of cyclic flow graphs, a noniterative algorithm has been developed for solving the material and energy balance equations of complex chemical-engineering systems.

Example VII-1. Develop material balances around a chemical-engineering system in which CO_2 is removed from synthesis gas by monoethanol amine.

(1) To begin with, we draw up a block-diagram of the process (Fig. VII-4). From this diagram, we then develop a flow graph (Fig. VII-5) in which the nodes represent the system units, and the arcs, the physical streams of the system.

This flow graph has two source nodes, $m = 2$; three sink nodes, $n = 3$; five intermediate nodes, $k = 5$, which represent the system units, and twelve arcs, $b = 12$.

Thus, the material flow graph has a total number of nodes equal to

$$v = m+n+k = 2+3+5 = 10$$

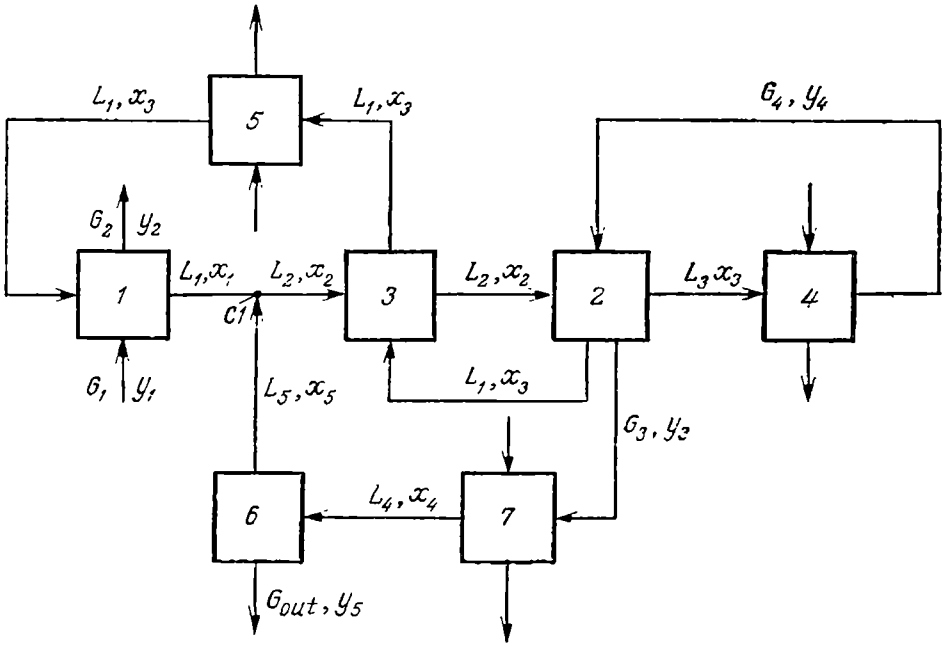

Fig. VII-4. Block-diagram of a chemical-engineering system for removal of CO_2 from synthesis-gas by monoethanol amine

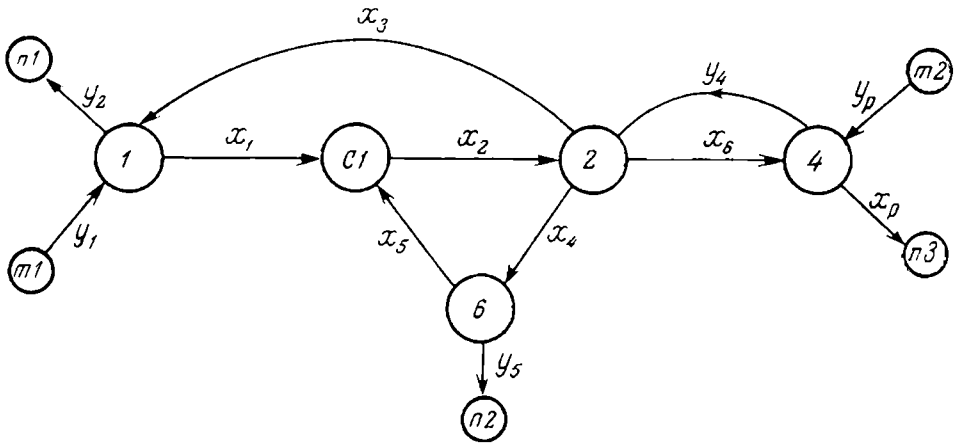

Fig. VII-5. Flow graph of the system in Fig. VII-4

(2) The next step is to draw up a cyclic flow graph, CFG (Fig. VII-6). In this graph:

(a) the number of nodes is

$$v_{CFG} = k+1 = 6$$

(b) the number of branches is:

$$e = b = 12$$

(c) the rank of the graph is

$$\rho = v_{CFG} - 1 = 5$$

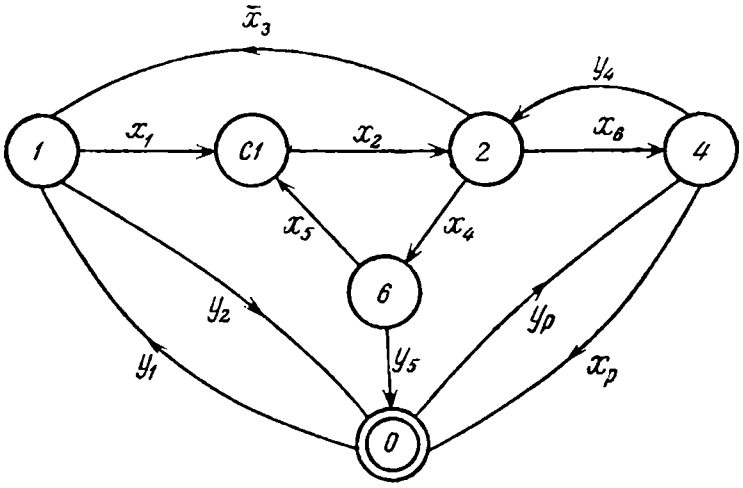

Fig. VII-6. Cyclic flow graph

(3) The number of branches in the tree of a cyclic flow graph is

$$e_t = \rho = 5$$

and the number of graph chords is

$$e_{ch} = e - e_t = 12 - 5 = 7$$

The chords are the following branches of the cyclic flow graph:

$$y_1, y_2, x_2, x_3, y_p, x_p, x_6$$

Now we construct the tree of the cyclic flow graph, the branches of which correspond to five base variables (Fig. VII-7):

$$x_1, x_4, x_5, y_4, y_5$$

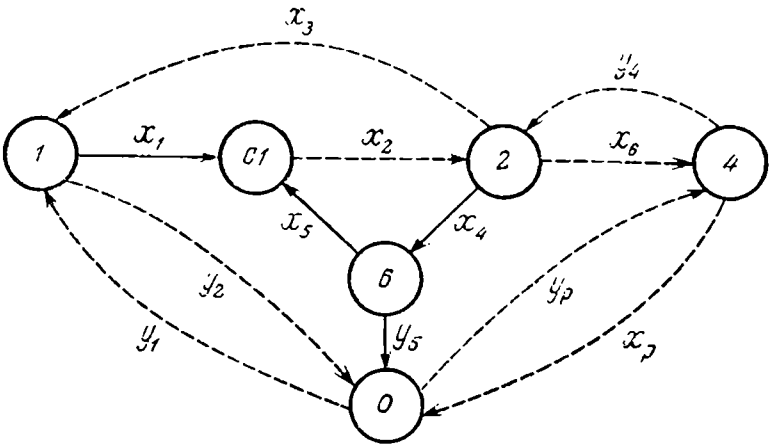

Fig. VII-7. Tree of a cyclic flow graph

(4) Now the fundamental cycles can be obtained (by connecting chords to the tree branches in ascending order of chord numbers: y_1, y_2, x_2, x_3, x_6, y_p, x_p):

$$\mu_1 = \{y_1, x_1, x_5, y_5\} \qquad \mu_5 = \{x_6, y_4\}$$
$$\mu_2 = \{y_2, y_5, x_5, x_1\} \qquad \mu_6 = \{y_p, y_4, x_4, y_5\}$$
$$\mu_3 = \{x_2, x_4, x_5\} \qquad \mu_7 = \{x_p, y_5, x_4, y_4\}$$
$$\mu_4 = \{x_3, x_1, x_5, x_4\}$$

(5) The following cyclomatic matrix in systematized form may be compiled for the CFG:

	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6	μ_7	
y_1	+1							
y_2		+1						
x_2			+1					
x_3				+1				
x_6					+1			
y_p						+1		$= [C]$
x_p							+1	
x_1	+1	−1		+1				
x_4			+1	−1		+1	−1	
x_5	−1	+1	+1	−1				
y_4					+1	+1	−1	
y_5	+1	−1				+1	−1	

(6) The relationships between the base and free variable flows may be written by adding together the row elements in the matrix $[C]$:

$$\begin{cases} x_1 = y_1 - y_2 + x_3 \\ x_4 = x_2 - x_3 + y_p - x_p \\ x_5 = y_2 - y_1 + x_2 - x_3 \\ y_4 = x_6 + y_p - x_p \\ y_5 = y_1 - y_2 + y_p - x_p \end{cases}$$

Substituting the specified values of free variables flows in the above equations will give the values of all other flows.

VII-2. CALCULATION OF CHEMICAL ENGINEERING SYSTEMS ON THE BASIS OF MATHEMATICAL MODELS OF SYSTEM ELEMENTS

As already noted, in an analysis of complex chemical-engineering systems one inevitably runs into considerable difficulties. Above all, these difficulties are associated with the specific structure of such systems (the use of recycles, cross, series and parallel flows) and the great number of dimensions involved. This makes imperative the search for engineering methods of design and optimization that would be efficient under the circumstances.

The design of a complex chemical-engineering system involves three tasks:

(1) Structural analysis of the system.

If an iterative computational procedure were applied to the entire system at once, the problem would involve a prohibitively large number of dimensions. It is the objective of structural analysis to reveal within the system feedback loops to which an iterative procedure could be applied on an independent basis. In this way, a problem involving a great number of dimensions can be reduced to a series of problems, each with a small number of dimensions.

A further important objective of structural analysis is to isolate an optimum (in a sense) set of flows that could be cut off in order to turn a closed into an open system which could be used as a basis for an iterative computational procedure. This, too, might reduce the number of dimensions involved.

(2) Search for an efficient iterative procedure.

It is common knowledge that the design of a closed chemical-engineering system is equivalent to solving a set of nonlinear finite equations. Therefore, an applicable iterative procedure must utilize the methods normally used to solve nonlinear equations, namely simple iteration, Newton's method, Wolf's method, etc. Thus, the objective of this task is to develop an iterative procedure that would ensure a fast convergence.

(3) Adaptation to computer solution.

At present, the most commonly used procedure in the calculation of chemical-engineering systems is firstly to solve consecutively mathematical models for component units and, secondly, to finalize the parameters of the material and energy flows between them. This approach is inapplicable, however, to chemical-engineering systems of an arbitrary structure. The point is that, should a system incorporate recycle, the time needed to run the problem on a digital computer would increase considerably, because iterations would have to be applied to all variables of the recycle flows. Since mathematical models take into account the spatial distribution of process variables, the time needed to calculate a chemical-engineering system increase still more.

By far the most efficient way to design and optimize a chemical-engineering system is to use operational matrices. In such a case, one sets up a matrix, $[C]$, for the constraint equations of the system. This matrix describes interrelations between all variables of the system and may be written as

$$[C]\,[X^{(1)}, X^{(2)}, \ldots, X^{(k)}, \ldots, X^{(N)}, Y_0]^* = 0 \qquad \text{(VII-20)}$$

where $X^{(k)}$ is the row-vector of the input varables of the kth unit; Y_0 is the row-vector of the output variables of the system, $[C]$ is the constraint-equation matrix whose elements correspond to those of the operational matrices, the "*" sign indicates transposition, and N is the number of units in the system. With Eq. (VII-20), there is no need to finalize the variables of the flows between the units by iteration.

In designing a chemical-engineering system, it is convenient to group its input variables into a separate vector, U, with the associated matrix $[B]$. Since, the output variables of the system (the vector Y_0) have no effect on the remaining variables, they may be calculated separately, after evaluation of the variables representing the internal relationships in the system. Then Eq. (VII-20) may be recast as follows

$$[C_1]\,[X_1^{(1)}, X_1^{(2)}, \ldots, X_1^{(k)}, \ldots, X_1^{(N)}]^* + [B_1]U = 0 \qquad \text{(VII-21)}$$

$$Y_0^* = [C_2]\,[X_1^{(1)}, X_1^{(2)}, \ldots, X_1^{(k)}, \ldots, X_1^{(N)}]^* + [B_2]U \qquad \text{(VII-22)}$$

where U is the column-vector of the input variables of the system, $X_1^{(k)}$ is the row-vector of the input variables of the kth element except the variables included in the vector, U, while $[C_1]$, $[C_2]$, $[B_1]$ and $[B_2]$ are the matrices of the respective constraint equations.

In optimizing an existing system, Eqs. (VII-21) and (VII-22) are solved repeatedly for a set of values of the components of the vector, U, so as to find optimum operating conditions for the system. This method may be used also to optimize the process and design variables of a system still being designed. Then the vector, U, is expanded to include variables expressing the engineering characteristics of units, the vector, D. Since the values of the process variables are unknown at the design stage, the initial approximation needed in order to carry out an experiment on a model may be derived from the material and heat balances developed by the process-operator method.

As a rule, in optimizing a chemical-engineering system, one needs only to know the output variables of the system (provided the input variables are specified in advance). Knowledge of process variables which characterize internal relationships in the system is not needed, because for most chemical-engineering systems the objective function may be defined as

$$\bar{R} = R(U, Y_0) \qquad \text{(VII-23)}$$

The time needed to solve Eqs. (VII-20) may be cut down through the use of signal flow graphs from which one can readily deduce an analytical expression for the input-output relationships of a system. A signal flow

graph is in fact a topological mapping of the system's constraint-equation matrix. The graph nodes represent the system variables, $[X^{(k)}, Y^{(k)}]$, and the arcs represent the relations between them, which are expressed by the coefficients of the constraint-equation matrix.

Using the rules of signal flow graph algebra, one can readily derive an analytical expression for the relations between the input variables, $[U]$, and the output variables, $[Y_0]$, of a system as

$$Y_0^* = [S]U \tag{VII-24}$$

where $[S]$ is the operational matrix of the system. Now the system can be analysed directly on the basis of Eq. (VII-24), thereby cutting down the computer time needed.

In cases where the constraint-equation matrix has a great number of dimensions, resort may be made to a method also based on the representation of system units in the form of operational matrices. Basically, this method consists in the successive reduction of the system's block diagram.

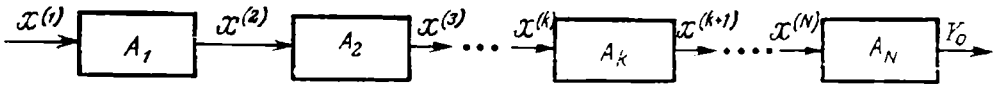

Fig. VII-8. Reacting vessels in series

For a group of N series-connected reacting vessels (Fig. VII-8), the input-output relationship may be expressed as

$$\begin{aligned} X^{(2)} &= [A_1]X^{(1)} \\ X^{(3)} &= [A_2]X^{(2)} \\ &\cdots\cdots\cdots\cdots \\ &\cdots\cdots\cdots\cdots \\ X^{(k+1)} &= [A_k]X^{(k)} \\ &\cdots\cdots\cdots\cdots \\ &\cdots\cdots\cdots\cdots \\ Y_0 &= [A_N]X^{(N)} \end{aligned} \tag{VII-25}$$

By expressing $X^{(k)}$ consecutively in terms of $X^{(k+1)}$, we get

$$Y_0 = [A_N][A_{N-1}] \ldots [A_k] \ldots [A_2][A_1]X^{(1)} \tag{VII-26}$$

If a system uses a recycle, it is convenient to isolate from the operational matrix of the unit receiving the recycle, a submatrix (H) which represents the relationship between the output variables and the recycle variables. Then, for a group of N units with recycle (Fig. VII-9), we get

$$Y_0 = \{(E-[A_N][A_{N-1}] \ldots [A_k] \ldots [A_2][H_1])^{-1} \ldots [A_N] \ldots [A_1]\}X^{(1)} \tag{VII-27}$$

where E is the unit matrix.

Using the above relations, one can readily derive an analytical expression for input-output relationships of most chemical-engineering systems.

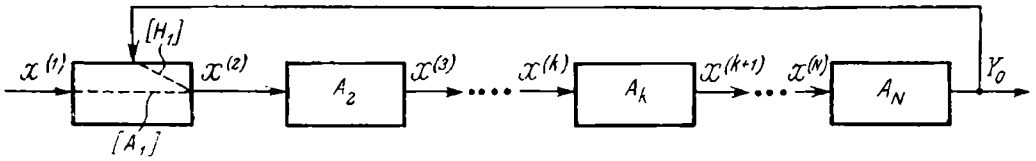

Fig. VII-9. Reacting vessels in series and with recycle

The use of constraint-equation matrices for analysis of a chemical-engineering system may be illustrated, taking as an example an absorption-desorption system in which carbon dioxide is removed from the gas with a solution of monoethanol amine. The block-diagram of the process appears in Fig. VII-10.

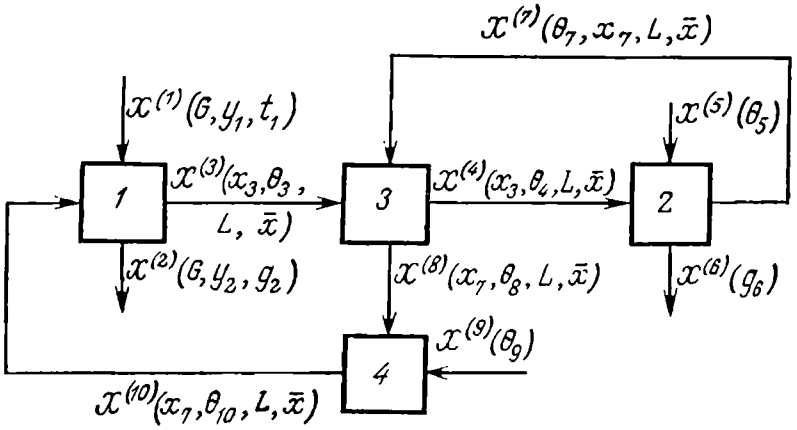

Fig. VII-10. Block-diagram of the process for removal of CO_2 with a solution of monoethanol amine

1 — absorber; *2* — regenerator; 6 — heat exchanger; *4* — cooler

For this system, the constraint equations, Eq. (VII-2) may be written as:

for the absorber

$$\begin{vmatrix} y_2 \\ \theta_3 \\ x_3 \\ g_2 \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} \\ a_{21} & a_{22} & \cdots & & & & a_{27} \\ a_{31} & \cdots & & & & & a_{37} \\ a_{41} & \cdots & & & & & a_{47} \end{vmatrix} \times \begin{vmatrix} G \\ y_1 \\ t_1 \\ L \\ \theta_{10} \\ x_{10} \\ 1 \end{vmatrix}$$

for the regenerator

$$\begin{vmatrix} \theta_7 \\ x_7 \\ g_6 \end{vmatrix} = \begin{vmatrix} b_{11} & b_{12} & b_{13} \ldots\ldots\ldots & b_{16} \\ b_{21} & b_{22} & \ldots\ldots\ldots\ldots & b_{26} \\ b_{31} & \ldots\ldots\ldots\ldots\ldots & & b_{36} \end{vmatrix} \times \begin{vmatrix} \frac{L}{x} \\ x_3 \\ \theta_4 \\ \theta_5 \\ 1 \end{vmatrix} \qquad \text{(VII-28)}$$

for the heat-exchanger

$$\begin{vmatrix} \theta_4 \\ \theta_8 \end{vmatrix} = \begin{vmatrix} d_{11} & d_{12} & d_{13} & d_{14} \\ d_{21} & d_{22} & d_{23} & d_{24} \end{vmatrix} \times \begin{vmatrix} L \\ \theta_3 \\ \theta_7 \\ 1 \end{vmatrix}$$

for the cooler

$$|\theta_{10}| = |c_{11} \quad c_{12} \quad c_{13} \quad c_{14}| \times \begin{vmatrix} \theta_9 \\ \theta_8 \\ L \\ 1 \end{vmatrix}$$

where G is the mass flow rate of the raffinate, L is the number of recycles for the solution of monoethanol amine, $\bar{x}$ is the concentration of the monoethanol amine solution, x_3 and x_7 are the concentrations of the active fraction of the absorbent in the saturated and regenerated solutions, g_2 and g_6 are the losses of the monoethanol amine solution in the absorber and regenerator, θ_5 and θ_9 are the energy (steam, cooling water) expended to sustain the process, t_1 is the gas temperature at the inlet to the absorber, θ_3, θ_4, θ_7, θ_8 and θ_{10} are the temperatures of the respective streams of the monoethanol amine solution.

Using the constraint equations, Eqs. (VII-28), for the individual processes, one can develop a matrix of constraint equations for the whole system. According to Eq. (VII-21), such a matrix may be written as

$$\begin{vmatrix} -1 & 0 & a_{25} & 0 & a_{26} & 0 & 0 \\ 0 & -1 & a_{35} & 0 & a_{36} & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & c_{12} \\ 0 & b_{13} & 0 & -1 & 0 & b_{14} & 0 \\ 0 & b_{23} & 0 & 0 & -1 & b_{24} & 0 \\ d_{12} & 0 & 0 & d_{13} & 0 & -1 & 0 \\ d_{22} & 0 & 0 & d_{23} & 0 & 0 & -1 \end{vmatrix} \times \begin{vmatrix} \theta_3 \\ x_3 \\ \theta_{10} \\ \theta_7 \\ x_7 \\ \theta_4 \\ \theta_8 \end{vmatrix}$$

$$+\begin{vmatrix} a_{21} & a_{22} & a_{23} & a_{24} & 0 & 0 & 0 & a_{27} \\ a_{31} & a_{32} & a_{33} & a_{34} & 0 & 0 & 0 & a_{37} \\ 0 & 0 & 0 & C_{13} & 0 & 0 & C_{11} & C_{14} \\ 0 & 0 & 0 & b_{11} & b_{12} & b_{15} & 0 & b_{16} \\ 0 & 0 & 0 & b_{21} & b_{22} & b_{25} & 0 & b_{26} \\ 0 & 0 & 0 & d_{11} & 0 & 0 & 0 & d_{14} \\ 0 & 0 & 0 & d_{21} & 0 & 0 & 0 & d_{24} \end{vmatrix} \times \begin{vmatrix} G \\ y_1 \\ t_1 \\ L \\ \bar{x} \\ \theta_5 \\ \theta_9 \\ 1 \end{vmatrix} = 0 \qquad \text{(VII-29)}$$

According to Eq. (VII-22), the following set of equations may be written in order to find the output variables of the system:

$$\begin{vmatrix} y_2 \\ g_6 \\ g_2 \end{vmatrix} = \begin{vmatrix} 0 & 0 & a_{15} & 0 & a_{16} & 0 & 0 \\ 0 & b_{38} & 0 & 0 & 0 & b_{37} & 0 \\ 0 & 0 & a_{45} & 0 & a_{46} & 0 & 0 \end{vmatrix} \times \begin{vmatrix} \theta_3 \\ x_3 \\ \theta_{10} \\ \theta_7 \\ x_7 \\ \theta_4 \\ \theta_8 \end{vmatrix} +$$

$$+\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} & 0 & 0 & 0 & a_{17} \\ 0 & 0 & 0 & b_{31} & b_{32} & b_{35} & 0 & b_{37} \\ a_{41} & a_{42} & a_{43} & a_{44} & 0 & 0 & 0 & a_{47} \end{vmatrix} \begin{vmatrix} G \\ y_1 \\ t_1 \\ L \\ \bar{x} \\ \theta_5 \\ \theta_9 \\ 1 \end{vmatrix} \qquad \text{(VII-30)}$$

The matrix, (VII-29), and the equations, (VII-30) may be directly utilized in the computational procedure which is carried out as follows:

(1) values are assumed for the independent input variables of the system (the vector U) and the set of linear algebraic equations, Eqs. (VII-29), is solved for the process variables (the vector X);

(2) using the values of the vector X, the set of equations, Eq. (VII-30), is solved for the output variables (the vector Y_0).

Among the advantages offered by constraint-equation matrices in the analysis of a system of interrelated units are accuracy, an all-embracing investigation of the system through the use of mathematical models for the individual processes, and the convenience of computer solution that is characteristic of the process-operator method.

System analysis based on the presentation of system elements in the form of operational matrices lends itself readily to automation both in the design

stage and in the study of existing systems, because the computational procedure is independent of the internal structure of the system and reduces to a non-iterative solution of sets of equations.

VII-3. MULTILEVEL OPTIMIZATION OF CHEMICAL ENGINEERING SYSTEMS

Of late, special emphasis has been placed on the search of methods to optimize complex chemical-engineering systems. With any method of optimization, the crucial point is the amount of computational work. This amount is especially formidable for closed systems with recycles, because a multitude of iterative steps have to be performed before the system's material and energy balances can be properly fitted. If we recall that in most cases a complex system is made up of a great number of interrelated units each described by an appropriate set of equations, and that in optimizing the problems have to be run on a computer more than once, it can readily be seen that, unless a way out is found, the demand on computer time may be anything but reasonable. A convenient way out is to decompose a multidimensional problem into a series of sub-problems with fewer dimensions.[2-4]

This can, for example, be done by optimizing a given chemical-engineering system at three consecutive levels as follows:

(1) the entire system is optimized for input and output variables of each region, which may be called diakoptic global optimization (DG-optimization);

(2) the various units or regions are optimized for the input and output variables of the individual units, which may be called regional optimization (R-optimization);

(3) each unit within a region is optimized, which may be called local optimization (L-optimization).

A problem may be taken as solved if the three levels are properly tied in by an iterative procedure.

The above class of methods also includes those based on the use of partial objective functions for subsystems and on a break-up of the overall problem into a series of sub-problems.

With the above methods, one of the more general descriptions of the system is used, assuming that fixed relationships exist between the subsystems. These relationships may be defined as

$$\bar{X}_i = \sum_{j=1}^{N} C_{ij}\bar{Z}_j \quad i = 1, \ldots, N \tag{VII-31}$$

where $\bar{X}_i$ represents the input vectors of the ith subsystem, $\bar{Z}_j$ represents the output vectors of the ith subsystem related to another subsystem, C_{ij} is a matrix consisting of zeros and units, and N is the number of subsystems.

It can readily be seen that Eqs. (VII-31) can describe all kinds of relationships that may exist in a complex system, except where parallel substructures exist.

Therefore, we may use the following equations which can describe all possible types of relationships:

$$\sum_{k=1}^{R_i} a_i^k \bar{X}_i^k = \sum_{j=1}^{N} C_{ij} \bar{Z}_j \quad i = 1, \ldots, N \tag{VII-32}$$

where R_i is the number of parallel loads in the ith substructure, k is the index of a given parallel load, and a is a matrix made up of zeros and units.

The objective function of the ith parallel substructure may be written as

$$F_i(\bar{X}_i, \bar{m}_i) = \sum_{k=1}^{R_i} F_i^k(\bar{X}_i^k, \bar{m}_i^k)$$

where $\bar{m}_i$ is the controlling vector.

The objective of optimization may be defined as

$$\begin{aligned} \max_{\bar{m}_i} \sum_{i=1}^{N} \sum_{k=1}^{R_i} F_i^k(\bar{X}_i^k, \bar{m}_i^k); \quad i = 1, \ldots, N \\ \sum_{k=1}^{R_i} a_i^k \bar{X}_i^k = \sum_{j=1}^{N} C_{ij} \bar{Z} \\ \bar{Z}_i^k = \bar{T}_i^k(\bar{X}_i^k, \bar{m}_i^k) \\ \bar{y}_i^k = \bar{S}_i^k(\bar{X}_i^k, \bar{m}_i^k) \\ G_i^k(X_i^k, m_i^k, y_i^k) \geq 0 \end{aligned} \tag{VII-33}$$

where X_i^k are the inputs, $\bar{Z}_i^k$ are the outputs directed to other subsystems, $\bar{y}_i^k$ are the outputs from the system as a whole, and m_i^k are the manipulated variables applied to the ith subsystem.

In multilevel approximation, the entire system is decomposed into a series of simplified subsystems which are then optimized independently of one another for a local objective function. In the final stage, all subproblem solutions are then coordinated to achieve a global optimum for the whole system.

Problems which differ from that defined by Eq. (VII-33) in the presentation of the relationships described by Eq. (VII-32) may be decomposed through use of Lagrange multipliers. Two methods have been developed, known as the "price" method and the "realizable (probabilistic)" method.

The Lagrangian expression for the problem described by Eq. (VII-33) has the form

$$\begin{aligned} L = \sum_{i=1}^{N} \Bigg[\sum_{k=1}^{R_i} F_i^k(\bar{X}_i^k \bar{m}_i^k) + \bar{\lambda}_i \Bigg(- \sum_{k=1}^{R_i} a_i^k \bar{X}_i^k + \sum_{j=1}^{N} C_{ij} \bar{Z} \Bigg) \\ + \sum_{k=1}^{R_i} \bar{\mu}_i^k (\bar{T}_i^k(\bar{X}_i^k \bar{m}_i^k) - \bar{Z}_i^k) \Bigg] \end{aligned} \tag{VII-34}$$

where $\bar{\lambda}_i$ and $\bar{\mu}_i^k$ are the Lagrange multipliers.

The necessary conditions that an optimum solution satisfies are as follows:

$$\frac{\partial L}{\partial \bar{m}_i^k} = \frac{\partial F_i^k(\bar{X}_i^k, \bar{m}_i^k)}{\partial \bar{m}_i^k} + \bar{\mu}_i^k \frac{\partial \bar{T}_i^k(\bar{X}_i^k, \bar{m}_i^k)}{\partial \bar{m}_i^k} = 0 \tag{VII-35}$$

$$\frac{\partial L}{\partial \bar{X}_i^k} = \frac{\partial F_i^k(\bar{X}_i^k, \bar{m}_i^k)}{\partial \bar{X}^k} + \bar{\lambda}_i a_i^k \bar{X}_i^k + \bar{\mu}_i^k \frac{\partial \bar{T}_i^k(\bar{X}_i^k, \bar{m}_i^k)}{\partial \bar{X}^k} = 0 \tag{VII-36}$$

$$\frac{\partial L}{\partial \bar{\mu}_i^k} = \bar{T}_i^k(\bar{X}_i^k, \bar{m}_i^k) - \bar{Z}_i^k = 0 \tag{VII-37}$$

$$\frac{\partial L}{\partial \bar{\lambda}_i^k} = \sum_{j=1}^{N} C_{ij} \bar{Z} - \sum_{k=1}^{R_i} a_i^k \bar{X}_i^k = 0 \tag{VII-38}$$

$$\frac{\partial L}{\partial \bar{Z}_i^k} = \sum_{j=1}^{N} \bar{\lambda}_j C_{ij}^k - \bar{\mu}_i^k = 0 \tag{VII-39}$$

It may be noted that the conditions from (VII-35) to (VII-37) make up subsystems, while the conditions, (VII-38) and (VII-39), are not separable. This circumstance may be utilized in order to decompose the problem into a two-level scheme, such that the subsystem problems, Eqs. (VII-35) through (VII-37), are solved at the first level, while at the second level the subsystem solutions are correlated through the use of Eq. (VII-38) or (VII-39).

According to which of the two last conditions is weakened at the first level, either the "price" method or the "realizable (probabilistic)" method is used.

The "price" method. If the Lagrange multipliers $\bar{\mu}_i^{k*}$ and $\bar{\lambda}_i^*$ are known and assuming that the condition, Eq. (VII-39), must be satisfied, the necessary and sufficient conditions, Eqs. (VII-35) through (VII-37), may be defined as

$$\begin{aligned}
\frac{\partial L}{\partial \bar{m}_i^k} &= \frac{\partial F_i^k(\bar{X}_i^k, \bar{m}_i^k)}{\partial \bar{m}_i^k} + \sum_{j=1}^{N} \bar{\lambda}_j^* C_{ji}^k = \bar{0} \\
\frac{\partial L}{\partial \bar{X}_i^k} &= \frac{\partial F_i^k(\bar{X}_i^k, \bar{m}_i^k)}{\partial \bar{X}} + \sum_{j=1}^{N} \bar{\lambda}_j^* C_{ji}^k \frac{\partial \bar{T}_i^k(\bar{X}_i^k, \bar{m}_i)}{\partial \bar{X}^k} - \bar{\lambda}_i^* a_i^k \bar{X}_i^k = \bar{0} \\
\frac{\partial L}{\partial \bar{Z}_i} &= \bar{T}_i^k(\bar{X}_i^k, \bar{m}_i^k) - \bar{Z}_i^k = \bar{0}
\end{aligned} \tag{VII-40}$$

Using Eq. (VII-40), we may solve the subsystem equations for $\bar{X}_i^k$, $\bar{m}_i^k$ and $\bar{Z}_i^k$, separately, taking arbitrary values for the Lagrange multipliers.

Since the solutions thus obtained satisfy all conditions for an optimum solution as a whole, except the condition, Eq. (VII-38), new values are found by trial and error for the Lagrange multiplier $\bar{\lambda}_i$ until the condition, Eq. (VII-38), is satisfied, too.

The iterative procedure used for this correlation may be defined as

$$\bar{\lambda}_i^{n+1} = \bar{\lambda}_i^n + \rho\left(\sum_{j=1}^{N} C_{ij} \bar{Z} - \sum_{k=1}^{R_i} a_i^k \bar{X}_i^k\right) \tag{VII-41}$$

where n is the iteration step.

The "realizable (probabilistic)" method. This method reduces to the following. One chooses arbitrary values of the interrelated variables $\bar{Z}_i^k$ already at the first level. However, the condition, Eq. (VII-38), is inseparable relative to the subsystems and, as a consequence, solutions for the subsystems cannot be obtained separately by direct application of the chosen values.

A way out is to use a special form of the interrelated equations, Eq. (VII-32). Consider the following problem

$$\max_{\bar{X}_i} \sum_{i=1}^{N} F_i(X_i)$$

$$\sum_{i=1}^{N} h_i(\bar{X}_i) \geqslant H \tag{VII-42}$$

and on introducing the correlating variables S_i such that the condition

$$\sum_{i=1}^{N} S_i \geqslant H \tag{VII-43}$$

is satisfied, the problem, Eq. (VII-42), may be decomposed into the following steps:

– the first step

$$\max_{\bar{X}_i} F_i(\bar{X}_i)$$

$$h_i(\bar{X}_i) = S_i \tag{VII-44a}$$

– the second step

$$\max_{S_i} \sum_{i=1}^{N} F_i(\bar{X}_i^0(S_i))$$

$$\sum_{i=1}^{N} S_i \geqslant H \tag{VII-44b}$$

It has been shown by several investigators that the use of Lagrange multipliers can simplify the second step because

$$\sigma_i = \frac{\partial \sum_{i=1}^{N} F_i(X_i^0(S_i))}{\partial S_i} \tag{VII-45}$$

where σ_i represents the Lagrange multipliers corresponding to Eq. (VII-34).

Then the condition, Eq. (VII-38), will take the form

$$\bar{X}_i^k - \bar{S}_i^k = \bar{0} \tag{VII-46}$$

and

$$\sum_{k=1}^{R_i} a_i^k \bar{S}_i^k = \sum_{j=1}^{N} \sum_{k=1}^{R_i} C_{ij}^k \bar{Z}_j^k \tag{VII-47}$$

Thus, the condition, Eq. (VII-38), is separated, and the first part of the problem can be solved. Since the initial values were chosen arbitrarily, corrections have to be made according to Eq. (VII-45), and this introduces an additional level.

The special linear form of interrelated equations makes it possible to use a relatively simple algorithm for the correlation step. Adjusted to satisfy Eq. (VII-47), this algorithm may be written as:

$$\bar{S}_i^{k(n+1)} = \bar{S}_i^{k(n)} + \rho\left(\bar{\sigma}_i^{k(n)} - \frac{1}{\sum_{k=1}^{R_i} a_i^k} \sum_{t=1}^{R_t} a_i^t \bar{\sigma}_i^t\right)^n \qquad \text{(VII-48)}$$

where $\bar{\sigma}_i^k$ are the Lagrange multipliers satisfying the condition (VII-46).

The second part of the correlation algorithm does not differ from that given earlier

$$\bar{Z}_i^{k(n+1)} = \bar{Z}_i^{k(n)} + \rho\left(\bar{\mu}_i^k + \sum_{j=1}^{N} \lambda_j^{(n)} C_{ij}^k\right) \qquad \text{(VII-49)}$$

In conclusion, it may be noted that there exist a great number of various methods for the design and optimization of chemical-engineering systems. As a rule, however, they are only applicable to a limited range of specific problems, which is explained by the complexity of the engineering and informational topology of systems.

This is why the development of design and optimization methods applicable to chemical-engineering systems of an arbitrary structure, however, complex, is an urgent task. This is also true of the decomposition of complex systems for the purpose of optimization.

A decisive step towards achieving the above goals can be made through systematic studies in the field of mathematical modeling and by compiling libraries of standard computer programs for unit processes of chemical engineering.

VII-4. COMPUTER-AIDED DESIGN OF CHEMICAL MANUFACTURE

Whether creating a new chemical manufacture or streamlining an old one, the last step in all experimental and research work is a design. The design of a chemical manufacture should bring into a sharp focus all latest advances in the field, embody present-day techniques for the synthesis of process lines from standard units, give consideration and a well-founded evaluation to all the alternate process and engineering approaches, and pick the best one.

Obviously, yesterday's techniques of design "by hand" can hardly cope with all of these tasks successfully. The most they can do is to examine a limited number of set-ups and layouts, doing so at the expense of prohibitively much time spent for the greater part in an attempt to tie in the designs

of the various parts of a process, carried out graphically. If we add to this that design work on a chemical manufacture must be completed in a very limited time and also that the number of projects in the chemical industry has been growing continually, we are forced to seek a fundamentally novel approach to the solution of the entire problem of design.

This approach comes with the use of computers.

As a global problem, the development of a computer-aided system for the design of chemical manufactures is inseparable from systems analysis, and both necessitate advances to new frontiers in science and technology. Inevitably, this changes scientific and organizational standards in (1) R&D activities towards faster and bigger payoffs; (2) design work; (3) the development of automatic control, management and information systems; and (4) chemical manufactures as entities of large unit capacities. Taken together, these factors offer an effective tool for developing fundamentally new self-contained chemical manufactures operating only under optimum conditions.

It is important to stress that computer-aided design is more than merely shifting design calculations onto a computer. This is a problem of paramount economic significance, centred around the designing of chemical manufactures on the basis of external feedback between R&D people and chemical factories. A computer-aided design system is a ramified cybernetical organism comprising the human designer engaged in a dialogue with the computer, in which he is assisted by subsystems for data search and retrieval, exchange with R&D and design people, and with chemical factories.

Thus, a computer-aided design system must incorporate a team of high-speed computers, a library of programs and data files, a team of mathematicians to update this library through intimate contact with R&D, design and production people, and R&D team, and a team of design engineers who do the actual design work in the light of their dialogue with the computers.

As an example, we shall take up a computer-aided system for the design of chemical (and petrochemical) manufactures. Typically, it will consist of:

– a subsystem supplying input data for the design of a chemical-engineering system;

– an information retrieval subsystem;

– a subsystem to model mathematically and optimize the chemical-engineering system being designed;

– an executive subsystem;

– a software subsystem;

– a subsystem to draw up graphs, diagrams, drawings and flow-sheets;

– a subsystem to present the final results of design work on the chemical-engineering system.

The design data input subsystem should contain all data on the process and information topology of the system being designed as a flow diagram, or a parametric flow graph, or an information flow graph; data on system throughput, composition and physical properties of source materials, inter-

mediate and end products; data on the process and design characteristics of the component units and of the chemical-engineering system as a whole; and requirements for the desired accuracy of design work.

These data can be read into the computer either on cards or in a free format. Each method has advantages of its own. With cards, the designer has to write pertinent data in a program language, and the number of documents that can thus be presented to the computer is very limited. With a free format, the engineer needs only to remember a few simple rules for the preparation of source data which may be named in any arbitrary manner. Free-format input is more flexible, but the designer has to write not only numerals, but also words, which means spending more time.

Data on the process and informational topology of a chemical-engineering system may be presented in the form of a parametric flow graph in which the labels for all nodes and edges of the graph make up a single system utilized in building mathematical models for the elements of the chemical-engineering system. In cases where the interest is in the effect that changes in process relationships may have on system performance, this technique is rather inflexible. A more attractive technique is to label separately the input and output flows of each element in a parametric flow graph, and to specify the process relationships by means of a topological matrix. The best choice in the respect is, however, the use of information-flow multigraphs, which are especially advantageous in solving optimization problems.

Data on the process streams of reactants and products in a chemical-engineering system can be presented as a matrix of the variables of these streams; data on the process and design characteristics of each element in the system as a matrix of the variables of a particular element type.

A simple and efficacious design-data input system may only be developed on the basis of a problem-oriented language specific to the design of chemical-engineering systems.

The information retrieval subsystem should contain the following catalogue and reference libraries:

– catalogue library covering the service characteristics of plant, standards and specifications of equipment, source materials and products for basic chemical (petrochemical) manufactures;

– a library of references on the reliability, process, technical and economical indices of existing chemical (petrochemical) manufactures;

– a library of references on the physico-chemical properties of materials used in basic chemical (petrochemical) manufactures;

– a library of references on the technical and economic indices of basic chemical (petrochemical) manufactures.

The information retrieval system can supply the data necessary for an optimum design solution based on the past experience of existing plants and units and tailored to the conditions prevailing in a given region.

The mathematical modeling and optimization subsystem will typically consist of the following functional units: a library of mathematical models

for typical chemical (petrochemical) processes; a library of mathematical models for elements of a large chemical-engineering system in modular form; a process straining unit; a process optimization and evaluation unit; a system element design variable straining unit; a system material and energy balance computing unit; a product cost finding unit; a physical-chemical unit conversion block; and a unit to compute the physical and chemical properties of the process streams in a chemical-engineering system.

The library of mathematical models for elements of a complex chemical-engineering system should be based on a modular principle which consists in the following. The mathematical model of each element is derived as a combination of the mathematical models of chemical (petrochemical) unit processes, or process operators. A module is a mathematical model of a process operator presented as a transformation matrix or a nonlinear functional expression. The library of mathematical models for elements of a chemical-engineering system in modular form may draw on the library of standard mathematical models for unit process operators and the operator flow diagram of the system.

A decision as to the accuracy of modules depends on whether the study is concerned with an individual element or a system as a whole. For example, a fairly accurate cost and economy model can be constructed for a system, using inaccurate modules for some system elements, provided these modules have a negligible effect on the accuracy of cost estimation for the system as a whole.

Since the desired accuracy of a mathematical model for each element is not known when design work is in its early stage, it is advantageous to try first simple modules in order to arrive at an approximate solution. Whether or not more accurate modules need be developed for some elements depends on the source data available, the final goal sought, and on how often a given module turns up in the design of different chemical-engineering systems. Sometimes, physico-chemical data on the process in question are inaccurate to a point where an attempt to build a more accurate module would have no sense. The modules that are used often in the design of different chemical-engineering systems should be built so that their simulation will take up a minimum of computer time.

Since the objective of design work is to predict how well the system in question will operate, it is important that arrangements be provided in modules for the correction and extrapolation of their variables under varying conditions. This requirement can readily be satisfied with modules based on the physico-chemical relationships of the process.

In the unit computing the physical properties for the process streams of a chemical-engineering system, the subprograms should preferably evaluate the physical properties of all streams on the basis of a minimum body of input data. For example, given molecular weight, boiling point under normal conditions and density, the subprograms should be able to determine enthalpy and vapour pressure, or to evaluate the physical properties of chemical compounds and mixtures on the basis of theoretical and exper-

imental data from regression equations. These subprograms should also be able to determine the dependent variables of process streams (such as heat capacity, density and viscosity) as functions of independent variables (mass flow rates, component concentrations, temperature and pressure).

The executive subsystem is a combination of several subprograms which coordinate the component subsystems of the computer-aided design system, keep watch on the modeling and optimization of the chemical-engineering system being designed, resolve this system into subordinate subsystems, map out an optimum flow of computation for elements in multiloop systems on the basis of a limited number of specific process variables, and guide the solution of equations describing the modules. The executive subsystem may utilize optimization algorithms for chemical-engineering systems based on topological models. Apart from the operations listed above, the executive subsystem should incorporate capabilities to change the process and informational topology of the system, to correct module variables, to change module types, and to display the results of system modeling in a simple and graphical manner.

In a way, the executive subsystem simulates a human coordinator who guides and supervises the design work on the entire chemical-engineering system by issuing orders, receiving reports from the various teams, and evaluating the pertinent data.

The software subsystem combines a library of subprograms for the analysis, synthesis and optimization of chemical-engineering systems, a library of subprograms ensuring the convergence of computational procedures, etc. The software subsystem must be continually and incessantly updated and improved.

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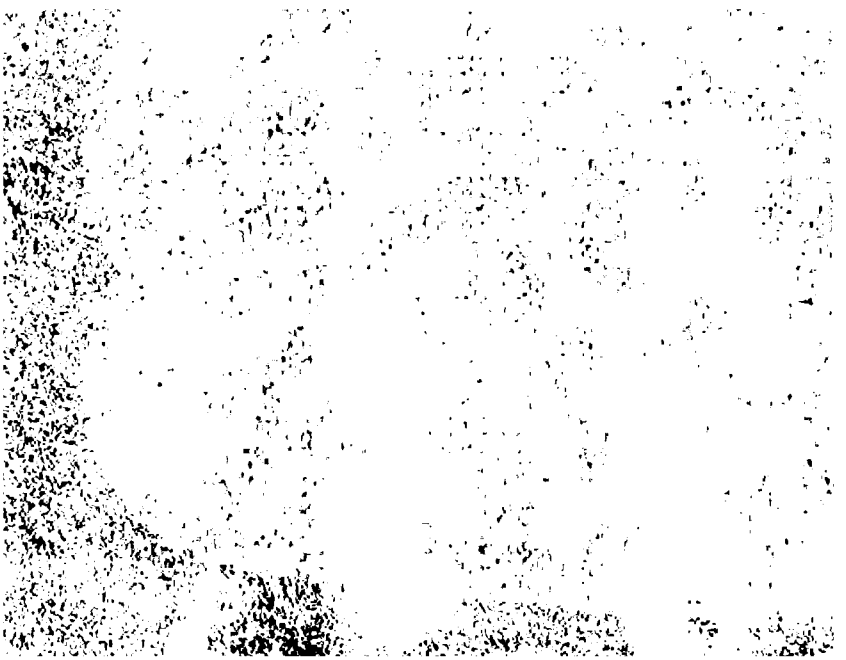
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